

DRAFT

**Great Lakes Binational Toxics Strategy
Octachlorostyrene (OCS) Report:
A Review of Potential Sources**

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**for
United States Environmental Protection Agency
Great Lakes National Program Office**

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EXECUTIVE SUMMARY

The *Canada-United States Strategy for the Virtual Elimination of Persistent Toxic Substances in the Great Lakes Basin* (Binational Toxics Strategy) challenges the United States to confirm by 1998 that there is no longer use or release from sources that enter the Great Lakes Basin of the industrial byproduct octachlorostyrene (OCS). Although OCS has recently been gaining attention because of its status as persistent, toxic, and bioaccumulative, very few government programs address this chemical. In particular, EPA has not previously compiled any inventory of sources and releases, regional or nationwide. This is likely due to the scarcity of data concerning the toxic effects of OCS in humans and the adverse effects on wildlife. Based on an extensive review of the literature, this report aims to characterize the potential sources, releases, and environmental loadings of OCS that may enter the Great Lakes Basin, identify whether sufficient information exists to confirm no use or release, and make recommendations for the Binational Toxics Strategy concerning OCS.

In the Great Lakes region, the St. Clair, Ashtabula, and Niagara rivers, in addition to tributaries to Lake Huron, are the sites of greatest OCS contamination. Sources at the head of the St. Clair River near Sarnia, Ontario, are suspected of contaminating Lake St. Clair and the Detroit River. Fish from Ashtabula, Ohio, where the Ashtabula River empties into Lake Erie, have been found to be highly contaminated with OCS. OCS-contaminated sediments from Lake Ontario have historically been correlated with the rise and fall of chlorine production along the Niagara River. Contamination of Lake Superior and Lake Michigan appears to be low, and what is there is thought to have resulted from long-range atmospheric transport.

OCS was first identified in Norway as a byproduct of magnesium production. It is now understood that OCS can be found in processes involving carbon and chlorine at high temperature, or with a high electrical flux, or processes involving aromatic compounds with chloroalkyl radicals. Initial sources of OCS identified in the U.S. involved the chlor-alkali industry, as carbon electrodes were used to electrolyze sodium chloride for production of chlorine and sodium hydroxide (NaOH, or caustic soda). Numerous chlor-alkali plants operated in the Great Lakes basin. Since most have converted to metal anodes, direct OCS process emissions, as measured by sediment levels at discrete locations, have dropped substantially. Landfill leachates from process residues still contribute OCS to the environment, but many of these will be handled under Superfund cleanup.

The release of OCS by the commercial production of chlorinated solvents as well as the incineration of PVC has been documented. Aluminum plasma etching and aluminum degassing methods have also been reported to generate OCS. A landfill used to dispose of chlorinated tars was found to be leaching OCS. Smelting operations to extract copper, nickel, niobium and tantalum, titanium, and vanadium have been implicated as sources of OCS. Additional processes identified as potential sources of OCS include secondary aluminum, copper, and lead smelting furnaces; fuel combustion and waste incineration processes; the production of ethylene dichloride/vinyl chloride; coke production; the manufacture of chlorinated phenols used in pesticides and wood preservation; bleaching processes and Kraft recovery furnaces in the wood

pulp and paper industry. In general, it appears that whenever hexachlorobenzene (HCB) and chlorinated dibenzodioxins (CDDs) are formed, there is potential that OCS is also formed.

Incineration, combustion, and metal smelting operations, as well as chlorinated solvents production, may produce significant levels of OCS. Due to the scarcity of data characterizing OCS emissions and the lack of national emissions estimates, an approximation of OCS emissions by source category was derived from U.S. national emissions estimates for CDDs and HCB. This exercise was conducted as a tentative gauge of OCS emissions for selected potential sources and is presented for discussion purposes only. This exercise suggests a potential U.S. OCS emissions rate of 4,000 lbs/year. Insufficient information exists to determine approximate emission levels for several documented sources of OCS, such as magnesium production, aluminum plasma etching, aluminum degassing, and niobium and tantalum extraction operations.

Lacking complete data, confirmation of no use or release of OCS from sources that enter the Great Lakes Basin cannot be made. Actions to verify potential sources, including monitoring of OCS in the environment, are recommended. In keeping with the Binational Toxics Strategy's emphasis on voluntary pollution prevention efforts, actions involving stakeholders to prevent, reduce, or eliminate the release of OCS in industrial processes may be undertaken simultaneously to reach the virtual elimination goal of the strategy.

In as much as OCS, chlorobenzenes, chlorostyrenes, chlorobiphenyls, chloronaphthalenes, and chlorinated dioxins and furans are formed concurrently in sources, these chlorinated compounds may have a cumulative effect more significant than that of OCS alone. OCS may serve as an effective marker compound for all of these compounds: it is a single isomer and is present at sufficiently high levels that analysis methods are not as costly or time-consuming as those for CDDs. In this way, an effective screening method may be developed. The reduction of OCS may indicate the simultaneous reduction of a range of co-generated compounds.

1.0 INTRODUCTION

Octachlorostyrene (OCS) is a persistent, bioaccumulative, and toxic chemical that is not deliberately manufactured but is produced as a byproduct in certain industrial processes. OCS is targeted as a Level I substance in the *Canada-United States Strategy for the Virtual Elimination of Persistent Toxic Substances in the Great Lakes Basin* (Binational Toxics Strategy). The challenge set out in the Binational Toxics Strategy for OCS in the U.S. is to:

Confirm by 1998 that there is no longer use or release from sources that enter the Great Lakes Basin of the industrial byproduct/contaminant octachlorostyrene. If ongoing, long-range sources from outside of the U.S. are confirmed, work within international frameworks to reduce or phase out releases of this substance.

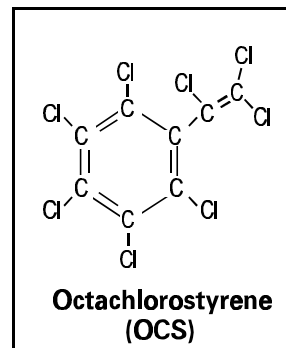
The purpose of the present report is to:

- # summarize the available information in the scientific literature that can be used to characterize the potential sources, releases, and environmental loadings of OCS entering the environment,
- # identify whether sufficient information exists to confirm no use or release,
- # make recommendations for next steps for the Binational Toxics Strategy, including opportunities to eliminate formation of OCS as a byproduct and assessment of the contribution of long range sources to OCS contamination in the Great Lakes Basin.

Concern over the occurrence of OCS in the environment is driven by two main factors: its persistence (i.e., very slow chemical and/or metabolic degradation) and its bioaccumulation (i.e., increase in concentration in higher order animals of a food chain). Potential, but largely unknown, human toxicological effects, as extrapolated from the effects of similar persistent chlorinated organic compounds, provide further rationale for action.

1.1 CHEMICAL STRUCTURE

OCS is a fully chlorinated styrene with the structure shown at right, and chemical formula C_8Cl_8 . A similar structure with eight hydrogen atoms in place of the eight chlorine atoms would constitute styrene, C_8H_8 . Polychlorinated styrenes (PCS) are the class of compounds containing between one and eight chlorine atoms substituted for hydrogen on the styrene backbone. Chlorinated styrenes other than OCS, ranging from one to seven chlorines with chemical formulae C_8H_7Cl to C_8HCl_7 , have been detected together with OCS in environmental samples and source emissions. Increasing chlorination increases both persistence and bioaccumulation, decreases water solubility, and increases lipid (fat) solubility. The



electronic resonance stabilization of the aromatic ring makes PCS compounds, and OCS in particular, resistant to biodegradation. That OCS is a highly persistent organic compound is based on its intrinsic thermodynamic stability (Norheim & Roald 1985).

1.2 STYRENE

Just as stable but lacking chlorine atoms, styrene (vinyl benzene) is an aromatic monomer that is readily polymerized to form commercially important styrene polymers. Polymerization methods vary. Spontaneous polymerization occurs when styrene is heated above about 105 °C. Chemical-initiated mechanisms in bulk, solution, suspension, and emulsion processes require lower temperatures, form fewer byproducts, and can improve the impact property of the resin.

Polystyrene is a thermoplastic commodity used mainly in packaging, appliances, furniture, toys, and housewares. It is also used in compact discs, in liners for refrigerators, and as foam for insulation. Worldwide, over 10 billion pounds of polystyrene are produced each year (Priddy 1996). In the U.S., 1993 sales of polystyrene resin reached 5.5 billion pounds, and growth has remained steady for several years (Sosa & Blackmon 1996).

Polystyrene resins are neither toxic to humans and wildlife nor harmful to the environment. Styrene, though, by virtue of the alkene double bond that can be metabolically converted to a reactive epoxide, has been identified as a suspected human carcinogen, responsible for leukemias and lymphomas in highly exposed workers. The incineration of polystyrene products, together with a source of chlorine, has the potential to form OCS, which is extremely persistent and bioaccumulative.

1.3 TOXICITY

Critical data have not been accumulated on the toxicity of OCS. Mammalian carcinogenicity and toxicity testing results are limited at this time; acute and chronic mammalian toxicity have been assessed in only single 28-day, 90-day and 12-month feeding trials in rats. Mutagenicity has been tested in only two Ames assays (Chu, 1982, 1984, 1986). Aquatic toxicity has been assessed with only one crustacean specie (Tarkpea, 1985).

The state of New York has adopted an acceptable daily intake rate (ADI) of 0.03 µg/kg per day (New York State Dept. of Environmental Conservation, 1997).

A human NOAEL (no observable adverse effect level) of 0.03 mg/kg/day has been suggested on the basis of the 12-month rat feeding study alluded to above. Primary adverse histological changes were found in the liver, kidneys, and thyroid, but the severity of the histological changes with respect to impairment in function was not well quantified. The changes in the liver were considered “moderate to severe” and the changes to kidneys and thyroid were “mild to moderate” (Chu, 1982, 1984, 1986). No treatment-related tumors were found in the 12-month feeding study, and OCS was not mutagenic in Ames bioassay tests (Tarkpea, 1985; Holme and Dybing, 1982).

However, OCS may act as a “promoter” of mutagenicity, and thus, possibly also a promoter of carcinogenicity. This promoter activity was determined from the enhanced mutagenicity of known mutagens when tested with OCS-activated rat liver enzymes. In addition, generalized toxicity of OCS may be inferred, in part, on the basis of its structural similarities to hexachlorobutadiene and hexachlorobenzene, both of which are toxic and carcinogenic (Holme and Dybing, 1982).

The aquatic toxicity LC_{50} of OCS has been established with the crustacean specie *Nitocra spinipes*. The OCS LC_{50} value of 0.068 mg/L for this specie falls within the range of other known chlorinated toxic compounds, with DDT at 0.030 mg/L and pentachlorophenol at 0.270 mg/L. These data tend to suggest a highly toxic compound for aquatic species.

The one study that suggests a link between OCS exposures and adverse human health effects is extremely speculative, and is not based on any direct measurements of workplace OCS levels, workplace exposures and/or potentially confounding factors. This particular epidemiological study reported that female workers at semiconductor production plants (where OCS is known to be produced, albeit captured and measured in vacuum pump oils used for mist control) have a higher risk of spontaneous abortion and deliver low-birth-weight infants (Schmidt et al. 1995). Further exposure assessment studies would be needed to be carried out before any greater weight-of-evidence significance is attached to these results.

1.4 BIOCONCENTRATION AND BIOACCUMULATION

The Bioconcentration Factor (BCF) is the ratio, at equilibrium, of the concentration in the tissues of an organism (e.g., fish) to water concentration when the concentration in the tissues comes only from water. The octanol:water partition coefficient can be a very good predictor for BCF tendencies, this due to the fact that the octanol:water interface mimics the interface between the water and the lipid-rich skin of the fish where partitioning occurs. A BCF value of 100,000 L/kg has been estimated for OCS from structure-activity relationships (Schulman and Klingele; 1985); this value suggests very low solubility of OCS in water and high degree of preference for a lipid-containing phase.

The BCF factor, though, does not take into account the biomagnification that occurs in a food chain, wherein increasingly higher concentrations of a persistent pollutant are measured in species of increasing trophic (feeding) level in a food chain. In contrast to the BCF, the Bioaccumulation Factor (BAF) is the ratio, at equilibrium, of the concentration in the tissues of an organism to water concentration when the concentration in the tissues comes from water *and* food. Thus, the BCF accounts for accumulation that occurs via direct contact with contaminated air, water and/or soil, *and* consumption of food. The BAF of OCS for trophic level 4 (highest level) fish is 117,500,000 L/kg and can be compared to BAFs for the pesticides *p,p'*-DDE and *p,p'*-DDT of 223,900,000 and 60,256,000 L/kg, respectively (Office of Water, US EPA; March 1995). The half-life for OCS, determined by transfer of contaminated eels from contaminated water to a clean water lake, was 790 days, or a little over two years (de Boer et al., 1994).

Oliver and Niimi (1988) investigated the biomagnification of OCS in the Lake Ontario ecosystem. The results of this study are depicted in Figure 1, where OCS concentrations were found to increase at each higher level of the food chain. The same study evaluated hexachlorobenzene (HCB) residues as well by trophic level, and found the same trends. However, the higher BAF of OCS, relative to HCB, resulted in sharply escalating ratios between these compounds, as OCS was observed to bioaccumulate to a greater extent in the upper level trophic fish. The effect of biomagnification in humans has not been determined. However, the OCS concentrations in the blood of residents near the Elbe River in Germany, where OCS has been measured in water, fish and sediments, have been correlated with fish consumption.

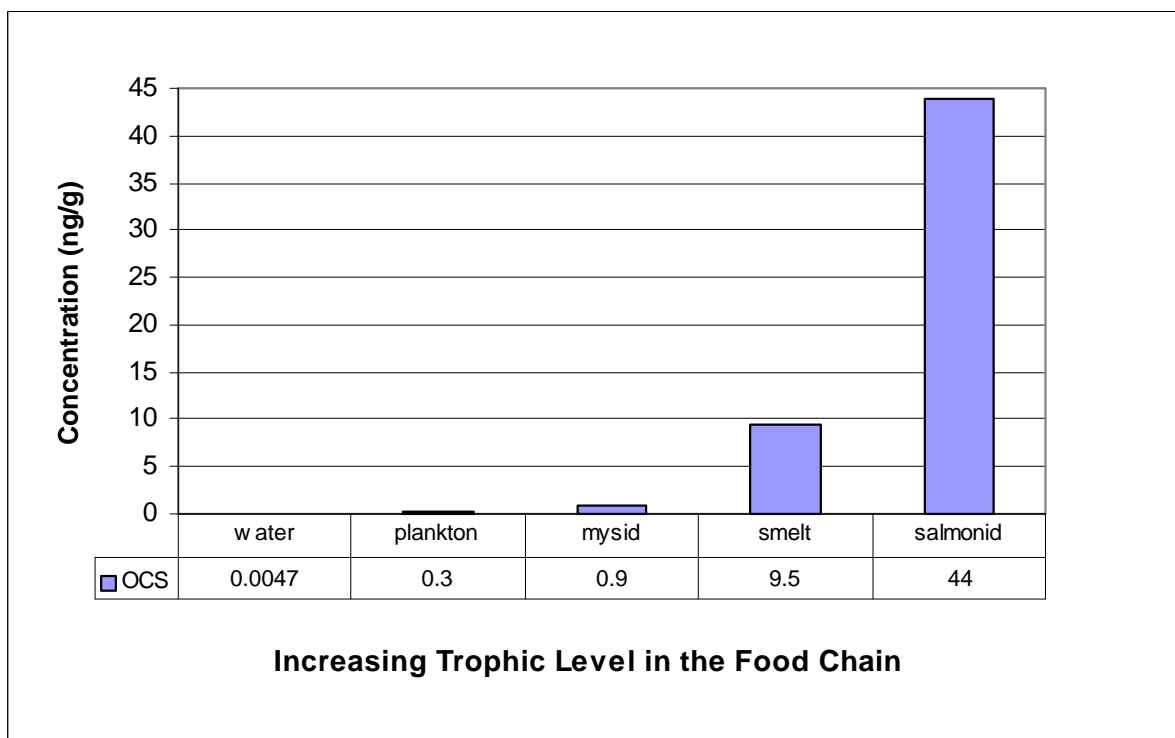


Figure 1. Comparison of OCS Concentrations in Lake Ontario Compartments

2.0 REGULATORY CONTEXT

2.1 REGISTRATION AND CLASSIFICATION STATUS OF OCS

OCS has been identified as a Level I substance in the United States Environmental Protection Agency (USEPA) Binational Toxics Strategy. OCS has not been identified specifically in any USEPA regulation and is not listed on the USEPA Register of Lists. The only USEPA program currently addressing OCS directly is the EPA Region 5 Water Division, which recognizes OCS as a Bioaccumulative Chemical of Concern (BCC) under the 1995 *Water Quality Guidance for the Great Lakes System* (GLI).

In its *Announcement of the Draft Drinking Water Contaminant Candidate List*, EPA identifies OCS as a suspected endocrine disruptor [Federal Register: October 6, 1997 (Volume 62, Number 193)]. Endocrine disruptors are chemicals that adversely affect the endocrine (i.e., hormonal) function of humans and wildlife. This effect is thought to harm male and female reproductive systems, cause thyroid damage, cause a range of other problems affecting developing fetuses and newborns, including low IQs, genital malformations, low sperm counts, and infertility, and possibly also cause cancer. EPA's Office of Prevention, Pesticides, and Toxic Substances (OPPTS) is currently engaged in research to demonstrate a relationship between exposure to suspected endocrine disrupting chemicals and associated adverse effects in humans. This research includes the development of a strategy to screen and test suspected chemicals.

The New York State Department of Environmental Conservation, Division of Water, has acknowledged the potential bioaccumulative and toxic properties of OCS by recommending limits for the protection of human health from consumption of OCS-contaminated water and fish. New York's recommended ambient water quality value for OCS for drinking water intake is 0.2 µg/L, and the recommended ambient water quality value for OCS based on human consumption of fish is 6×10^{-6} µg/L (New York State Department of Environmental Conservation, 1997).

In Canada, OCS is listed as a Tier 1 chemical under the 1994 *Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem* (COA).

2.2 RELEVANT DOMESTIC AND INTERNATIONAL PROGRAMS

Historically, OCS has not been included in the major monitoring or programmatic efforts directed at persistent, bioaccumulative toxics. For example, since 1990, the Integrated Atmospheric Deposition Network (IADN) Program, a joint Canada-U.S. monitoring and research effort mandated by the 1987 Great Lakes Water Quality Agreement, has monitored the atmospheric deposition of selected persistent chemicals, such as DDT and chlordane, at various locations throughout the Great Lakes. A three-tiered list of chemicals, intended to represent a spectrum of persistent toxic substances, was used to prioritize the initial investigations of IADN. According to the January 1998 *Technical Summary of Progress under the IADN 1990-1996*, monitoring for all of the 17 chemicals on the first two tiers, except mercury, has been successfully implemented. OCS was not included on the initial three-tier list. Similarly, OCS

has not been included in the global agreement on persistent organic pollutants (POPs), in EPA's Industrial Combustion Coordinated Rulemaking (ICCR), or in the monitoring of effluents under the National Pollutant Discharge Elimination System (NPDES).

However, OCS has been receiving more attention recently. Although not currently included in USEPA's Toxics Release Inventory (TRI), OCS is currently being considered for addition to the list of chemicals required for TRI reporting. In addition, an amendment to lower the TRI reporting threshold for persistent bioaccumulative chemicals, including OCS, has been proposed recently. OCS has been included as one of the twelve priority persistent, bioaccumulative, and toxic (PBT) substance in USEPA's evolving National PBT strategy. The absence of formal programs directed toward OCS releases is likely the result of insufficient information regarding its sources, releases, and loadings, and the potential hazards of exposure for humans and aquatic species.

Internationally, the OSPAR Commission for the Protection of the Marine Environment of the North-east Atlantic is committed to reducing discharges, emissions and losses of toxic, persistent, and bioaccumulative (hazardous) substances in the environment to achieve concentrations near background values for naturally occurring substances and close to zero for man-made synthetic substances by the year 2020, emphasizing the "precautionary principle". The OSPAR Commission is the joining of the former Oslo and Paris Commissions, adopting and continuing all recommendations and agreements entered into by those conventions. Although OCS is not on OSPAR's List of Chemicals for Priority Action, the commission will develop a selection and prioritization mechanism to first address chemicals of most concern, including those with the potential to act as endocrine disruptors. OSPAR has also identified, for the purpose of the development of programs and measures, sectors that are many of the same industries comprising potential sources of OCS. Further, OSPAR stated its intention to work with international organizations, including those undertaking clean-up of the rivers Rhine and Elbe, areas of documented OCS contamination (Internet address <http://www.ospar.org>).

3.0 PRESENCE OF OCS IN THE ENVIRONMENT

3.1 HISTORY OF ENVIRONMENTAL OCS DETECTION

Octachlorostyrene was first reported in 1969 in ducks of the Rhine River in the Netherlands (Koeman et al. 1969). In 1977, OCS contamination of Norwegian fjords was traced to the wastewater of a magnesium-producing plant in Norway, and OCS was discovered in the blood of employees of this plant (Lunde & Bjorseth 1977). In the same year, residues of OCS and heptachlorostyrene isomers (C_8HCl_7) were identified in Great Blue herons from Lake St. Clair. This was the first reporting of polychlorinated styrene (PCS) residues in the United States (Reichel et al. 1977). In 1984, “taffy tar” generated by graphitic anodes used in the production of chlorine was targeted as one primary source of OCS in the Great Lakes region (Kaminsky and Hites 1984).

The migration of OCS through the environment, and its impact upon human populations, was determined when a 1986 investigation revealed OCS in the breast milk of women from the Canadian Province of Ontario (Mes et al. 1993). While all sources of OCS contributing to this exposure were not known, the general consensus was that the high degree of OCS bioaccumulation was leading to its detection in higher trophic order species, such as humans. Similarly, in 1987, the milk of cows residing on farms in the vicinity of an incinerator and a chlorinated products plant was found to contain OCS (Rappe et al. 1987).

Since the time of the initial detection of OCS and other PCS in the environment, numerous studies have been conducted to investigate the occurrence, fate, and transport of OCS in areas of suspected contamination and to document the uptake by aquatic life and land-based organisms. The most notable areas of intense OCS/PCS studies are the Elbe Estuary in Germany, the River Rhine in The Netherlands, the North Sea between Britain and Norway, the Frierfjord in Norway, the Great Lakes Basin at the US/Canadian border, and the Bayou d’Inde area of southern Louisiana.

The body of evidence implicating these areas and industrial processes originated with studies conducted in the early 1980s. More recent evidence has identified other areas of OCS contamination as well. In 1994, OCS was commonly detected in food samples collected from farms and gardens of Flix, Spain, where the village is situated near a chlorinated organic solvent factory (Otero & Grimalt 1994). OCS was also found in the air above and in the sediments below the water reservoir where aqueous effluents of this solvent factory were released. In 1996, the presence of chlorinated organic compounds in river and tap water of this area was investigated again (Amaral et al. 1996). OCS, as well as HCB, were found to be major species in the river water and were found only at stations affected by discharges from the factory. Neither compound was detected in the village tap water, which is taken from a point upstream from the factory.

In the United States, sites not previously associated with OCS contamination have been reported recently. A 1995 report of contaminants in dolphins suggested a source of OCS on the

Texas coast (Kuehl and Haebler 1995). Corpus Christi Harbor, Texas, was listed as one of the sites of highest OCS contamination in the U.S. a year earlier (Kuehl and Butterworth 1994). Although Lake Ontario, and other Great Lakes, have documented levels of OCS in water, fish and sediment, Metcalfe and Charlton recently (1990) identified OCS in native mussels of the St. Lawrence River. Detection of OCS in this river outflow from Lake Ontario suggests either longer range transport and deposition than previously expected, slow release and migration from the pooled contamination areas around the Niagara River and Lake Ontario, and/or direct input from sources along the river. *In toto*, the results of these studies suggest that despite increased regulatory actions taken over the last decade to limit effluent discharges of potentially hazardous chemicals, these materials are probably still being formed, and are still being released into the environment.

3.2 MEASURED CONCENTRATIONS OF OCS IN THE GREAT LAKES REGION

In the Great Lakes region, the St. Clair, Ashtabula, and Niagara rivers, in addition to tributaries to Lake Huron, are the sites of greatest OCS contamination in the environment. Sources at the head of the St. Clair River near Sarnia, Ontario, are suspected of contaminating Lake St. Clair and the Detroit River. Fish from Ashtabula, Ohio, where the Ashtabula River empties into Lake Erie, have been found to be highly contaminated with OCS, with tissue levels reaching 405 ng/g. OCS-contaminated sediments from Lake Ontario have been correlated with the rise and fall of chlorine production along the Niagara River. Minor contamination of Lake Superior is thought to have resulted from atmospheric transport of OCS from Lake Ontario, although this would not explain the high concentrations detected in the Upper St. Marys River. OCS levels in Lake Michigan have been reported to be very low.

Since the discovery of OCS in the Great Lakes in the late 1970s, numerous studies have been undertaken to detect and quantify OCS contamination in the water, sediment, and aquatic life of this region. Table 1 summarizes measured concentrations of OCS in the Great Lakes and tributaries such as the Niagara River, Lake St. Clair (between Lakes Huron and Erie), and the St. Clair and Detroit Rivers.

Table 1. OCS in the Great Lakes System

Measured Concentrations of OCS				
Year¹	Concentration	Medium	Location	Reference
Lake Superior				
1983	205* ng/g	carp	Upper St. Marys River (Lake Superior tributary)	Jaffe et al. 1985
1983	17.7* ng/g	lake trout and whitefish	Siskiwit Lake, Isle Royale	Swackhammer & Hites 1988
1983	6.8 ng/g	carp	Keweenaw Bay	Jaffe et al. 1985
1980	ND, <1 ng/g	lake trout	Copper Harbor, MI	Kuehl et al. 1981
1974	ND, <1 ng/g	lake trout	Apostle, Islands, WI	Kuehl et al. 1981
Lake Michigan				
1980	ND, <1 ng/g	lake trout	Grand Traverse Bay	Kuehl et al. 1981
Lake Huron				
1980	.02-0.1, 0.06* ng/g	sediment	Southern Lake Huron	Oliver & Bourbonniere 1985
1983	1350* ng/g	carp	Tittabawassee River (Lake Huron tributary)	Jaffe et al. 1985
1983	970* ng/g	carp	Saginaw Bay (Lake Huron tributary)	Jaffe et al. 1985
1983	930 ng/g	carp	Chippewa River (Lake Huron tributary)	Jaffe et al. 1985
1983	695* ng/g	carp	Saginaw River (Lake Huron tributary)	Jaffe et al. 1985
1983	460 ng/g	carp	Shiawassee River (Lake Huron tributary)	Jaffe et al. 1985
1983	250* ng/g	carp	Flint River (Lake Huron tributary)	Jaffe et al. 1985
1983	120 ng/g	carp	Thunder Bay River (Lake Huron tributary)	Jaffe et al. 1985
1983	96 ng/g	carp	Au Sable River (Lake Huron tributary)	Jaffe et al. 1985
1980	110.7 ng/g	catfish/carp	Saginaw Bay, MI	Kuehl et al. 1981
1974	ND, <1 ng/g	chub	Mackinac, MI	Kuehl et al. 1981
Lake St. Clair and St. Clair & Detroit Rivers				
~1996	23.9 ng/g	sediment	Trenton Channel (mouth of Detroit River)	Drouillard et al. 1996
1987-1989	ND	suspended sediment	Point Edward, head of St. Clair River	Chan 1993
1987-1989	1.2-108.6, 21.1* ng/g	suspended sediment	Port Lambton, lower St. Clair River	Chan 1993

Table 1. OCS in the Great Lakes System (Continued)

Measured Concentrations of OCS				
Year ¹	Concentration	Medium	Location	Reference
1983	14.8 ng/g	sediment	St. Clair River	Pugsley et al.1985
1983	2.7 ng/g	sediment	Lake St. Clair	Pugsley et al.1985
1983	1.0 ng/g	sediment	Detroit River	Pugsley et al.1985
1982	5.1-11 ng/g	sediment	Lake St. Clair	Oliver & Bourbonniere 1985
1987-1989	0.02* ng/L	water	Point Edward, head of St. Clair River	Chan 1993
1987-1989	0.13* ng/L	water	Port Lambton, lower St. Clair River	Chan 1993
~1989	ND, <1 ng/L	stormwater	Sault Ste. Marie	Marsalek & Ng 1989
~1989	ND, <1 ng/L	stormwater	Windsor	Marsalek & Ng 1989
~1989	1.9 ng/L	stormwater	Sarnia	Marsalek & Ng 1989
~1989	254 ng/L	pt. source equivalent	Sarnia	Marsalek & Ng 1989
1986	210 ng/L	water	Treated leachate from Dow Chemical landfill	King & Sherbin 1986
1986	38, 160 ng/L	water	Dow Chemical sewers in Sarnia area	King & Sherbin 1986
1986	2.0 ng/L	water	Final effluent of Esso Chemical Canada	King & Sherbin 1986
1986	2.6, 4.2 ng/L	water	Township Ditch in industrial area of Sarnia	King & Sherbin 1986
1982-1983	1-2 ng/L	water	St. Clair River	Kauss & Hamdy 1985
1982-1983	ND, <1 ng/L	water	Detroit River	Kauss & Hamdy 1985
~1996	48.7 ng/g	mayfly nymphs	Trenton Channel (mouth of Detroit River)	Drouillard et al. 1996
1986	415.4 ng/g	aquatic insects	St. Clair River at Sarnia	Ciborowski & Corkum 1988
1986	140.4 ng/g	aquatic insects	lower St. Clair River	Ciborowski & Corkum 1988
1986	27.8* ng/g	aquatic insects	Detroit River	Ciborowski & Corkum 1988
1985-1986	84.8* ng/g	fish	Lambton Generating Station, St. Clair River	Suns & Hitchin 1992
1986	43* ng/g	fish	South Channel (St. Clair River delta)	Suns & Hitchin 1992
1986	3-5 ng/g	fish	Sturgeon Bar, MI (mouth of Detroit River)	Suns & Hitchin 1992
1986	85.6/115.3 ng/g	resident redheads/mallards	Walpole Island, Ontario (St. Clair River delta)	Hebert et al. 1990

Table 1. OCS in the Great Lakes System (Continued)

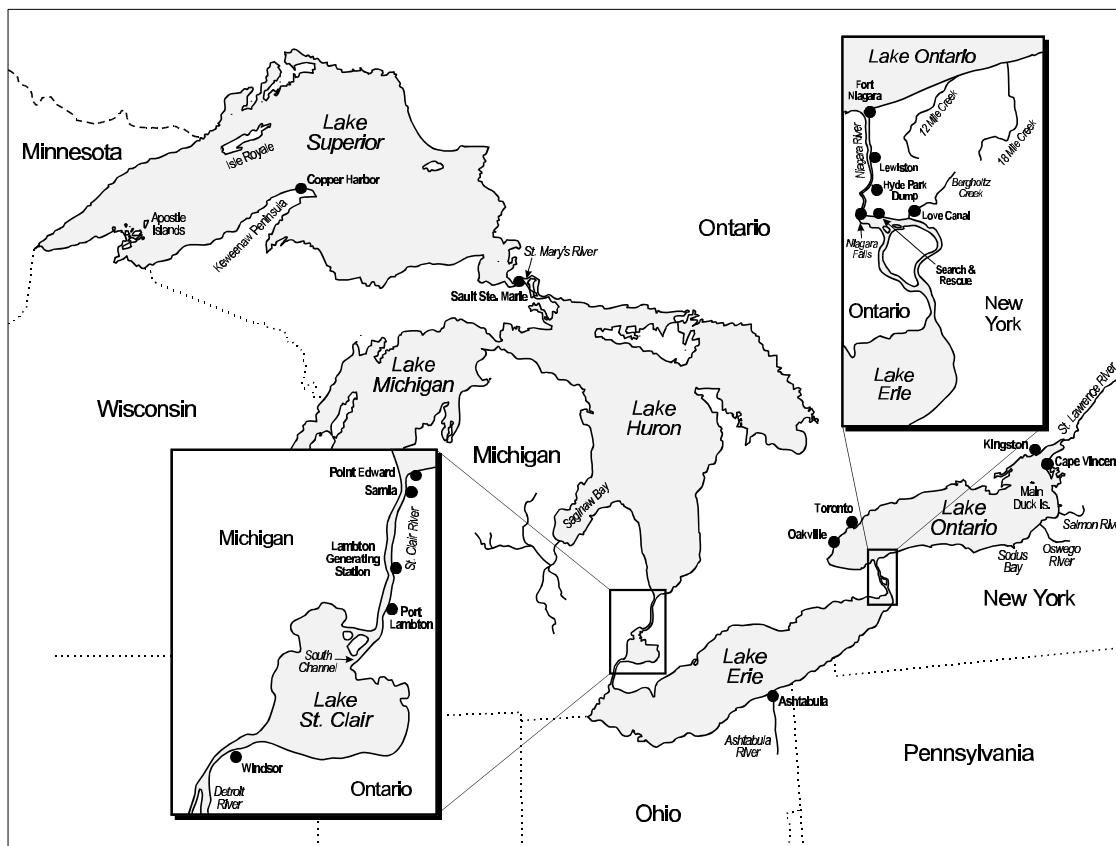
Measured Concentrations of OCS				
Year¹	Concentration	Medium	Location	Reference
1986	18.9/56.1 ng/g	migratory redheads/mallards	Walpole Island, Ontario (St. Clair River delta)	Hebert et al. 1990
1983	43.3 ng/g	clams	Lake St. Clair	Pugsley et al. 1985
1983	48.7 ng/g	clams	Detroit River	Pugsley et al. 1985
1982	55 ng/g	clams	St. Clair River near Sarnia	Kauss & Hamdy 1985
1982	29 ng/g	clams	St. Clair River at Port Lambton	Kauss & Hamdy 1985
1982	1-4 ng/g	clams	Detroit River	Kauss & Hamdy 1985
1980	227 ng/g	carp	Anchor Bay, MI, Lake St. Clair	Kuehl et al. 1981
1973	ND, 10, 60, 230 ng/g	Blue Heron eggs	Lake St. Clair, MI	Reichel et al. 1977
1970	390, 430 ng/g	Blue Heron carcass	Lake St. Clair, MI	Reichel et al. 1977
Lake Erie				
1982	0.8-5.9 ng/g	sediment	Western Lake Erie	Oliver & Bourbonniere 1985
1980	33.8 ng/g	carp	Woodtic, MI	Kuehl et al. 1981
1980	184 ng/g	carp/bass	Fields Brook, Ashtabula, OH	Kuehl et al. 1981
1979	256 ng/g	sucker	Fields Brook, Ashtabula, OH	Kuehl et al. 1981
1979	405 ng/g	Northern pike	Ashtabula River, Ashtabula, OH	Kuehl et al. 1981
1978	152 ng/g	sucker/roller/carp	Ashtabula River, Ashtabula, OH	Kuehl et al. 1981
1976	144 ng/g	5-species composite	Ashtabula River, Ashtabula, OH	Kuehl et al. 1981
Lake Ontario				
1981	4.3 ng/g	sediment	near Niagara River	Durham & Oliver 1983
1981	11 ng/g	bottom sediments	all Lake Ontario basins	Oliver & Niimi 1988
1993	31.3 ng/g	lake trout	Main Duck Island, eastern Lake Ontario	Huestis et al. 1996
1984	900 ng/g	carp	18 Mile Creek (Lake Ontario tributary)	Jaffe & Hites 1986
1984	650 ng/g	carp	Bergholtz Creek (Niagara River tributary)	Jaffe & Hites 1986
1984	410 ng/g	carp	Fort Niagara (mouth of Niagara River)	Jaffe & Hites 1986

Measured Concentrations of OCS				
Year ¹	Concentration	Medium	Location	Reference
1984	35 ng/g	carp	Oswego River (Lake Ontario tributary)	Jaffe & Hites 1986
1984	480 ng/g	carp	St. Lawrence	Jaffe & Hites 1986
1982	4.5* ng/g	spottail and emerald shiners	Search & Rescue, NY, Niagara River	Suns & Hitchin 1992
1981	3 ng/g	spottail shiners	Niagara River	Suns et al. 1983
1977	263 ng/g	lake trout	Main Duck Island, eastern Lake Ontario	Huestis et al. 1996
1977	281 ng/g	lake trout	Cape Vincent, NY (eastern Lake Ontario)	Kuehl et al. 1981

¹Indicates year samples were taken.

*Indicates an average (mean) of several samples.

ND = not detected, less than method detection limit when provided by author.



Huron-Erie Corridor

The Huron-Erie corridor flows from Lake Huron, down the St. Clair River to Lake St. Clair and through the Detroit River to Lake Erie. Pugsley et al. (1985) sampled surface sediments along the Huron-Erie corridor and suggested that the primary source of OCS is in the St. Clair River, downstream from Sarnia. This conclusion was drawn from the spatial distribution pattern of OCS in the sediments. The highest OCS levels in the corridor were in the sediments of the St. Clair River (14.8 ng/g), with similarly high levels extending out from the river delta, and lower levels in the center of Lake St. Clair (2.7 ng/g) and in the Detroit River (1.0 ng/g).

Comparable levels of OCS contamination were found in Lake St. Clair sediments (5.1-11 ng/g) by Oliver and Bourbonniere (1985), who also concluded that the primary source for OCS must be the St. Clair River. They reported low levels of OCS in sediment from southern Lake Huron (0.02-0.1 ng/g), leading into the St. Clair River, but higher levels of OCS in western Lake Erie sediments at the receiving end (0.8-5.9 ng/g).

Greater evidence of the origin of OCS contamination along the St. Clair River is reflected in measurements taken at Point Edward, located on the southern shores of Lake Huron at the head of the St. Clair River, as well as downstream at Port Lambton, at the mouth of the St. Clair River (Chan 1993). Mean values for water samples collected from 1987 to 1989 at the two sites were 0.02 ng/L and 0.13 ng/L, respectively. In sediment samples, OCS was not detected upstream at Point Edward, but was reported at a mean value of 21.1 ng/g at Port Lambton, indicating significant sources along the St. Clair River contributing to the OCS contamination of the Huron-Erie corridor.

Kauss and Hamdy (1985) further demonstrated this emerging spatial trend for OCS. They detected OCS in the St. Clair River (1-2 ng/L), but the pollutant was notably absent from the Detroit River. Moreover, the study indicated that the OCS found in the St. Clair River was mainly restricted to a narrow band along the Ontario side of the river where plumes from multiple sources in the Sarnia area were released.

Sarnia, Ontario, located on the Upper St. Clair River, contains numerous chemical and petrochemical industries whose effluents discharge into the St. Clair River. Marsalek and Ng (1989) examined pollutant loadings from nonpoint sources (i.e. urban runoff) in the Sarnia area. They report OCS (1.9 ng/L) in stormwater from the city of Sarnia but not in stormwater samples from Sault Ste. Marie and Windsor. They also calculated a mean point source equivalent (254 ng/L) that is comparable to point source loadings reported by King and Sherbin (1986) for industrial and municipal sources in the Sarnia area discharging to the St. Clair River. King and Sherbin (1986) measured 210 ng/L OCS in the treated leachate from a Dow Chemical landfill, and 160 ng/L and 38 ng/L OCS in samples collected from Dow Chemical's sewers. OCS was also discovered in trace quantities in Esso Chemical's effluent and in the Township Ditch, which receives local industrial discharges and landfill runoff.

As a result of the discharge of low levels (ng/L) of this persistent, bioaccumulative chemical, OCS has been repeatedly identified in aquatic life along the Huron-Erie corridor.

In 1970, OCS was detected in two of three (390 and 430 ng/g) Blue heron carcasses from Lake St. Clair, Michigan (Reichel et al. 1977). The same study reports OCS in Blue heron eggs collected from the same location in 1973 ranging from non-detectable levels to 230 ng/g. OCS was detected at a level of 227 ng/g in carp caught in Lake St. Clair at Anchor Bay, Michigan in 1980 (Kuehl et al. 1981). By comparison, fish caught in upper Lake Huron, at Mackinac, Michigan, in 1974 were not contaminated with OCS, while carp from Saginaw Bay, Lake Huron (in the “thumb” of lower Michigan), were reported to contain 110.7 ng/g OCS in 1980. Lower levels of OCS (33.8 ng/g) were found in carp caught in western Lake Erie at Woodtic, Michigan in 1980 (Kuehl et al. 1981).

Jaffe et al. (1985) further investigated the OCS contamination in Saginaw Bay, Lake Huron. In 1983, they analyzed fish (nearly all carp) from tributaries of Lake Huron at Saginaw Bay. High concentrations of OCS were discovered in carp of the Tittabawassee River (1350 ng/g), Saginaw Bay at the mouth of the Saginaw River (970 ng/g), and the Chippewa River (930 ng/g). Somewhat lower levels of OCS were found in fish from the Saginaw River (695 ng/g), the Shiawasse River (460 ng/g), the Flint River (250 ng/g), and Pine River (57 ng/g). OCS levels in fish from other tributaries which do not flow into Saginaw Bay but which contribute to the OCS contamination of Lake Huron were 120 ng/g at Thunder Bay River and 96 ng/g at Au Sable River.

In the 1980s, several studies reporting the accumulation of OCS in fish, ducks, and other aquatic life of the St. Clair and Detroit Rivers reinforced assumptions about sources of OCS along the upper St. Clair River. OCS contamination of clams collected from a clean lake and introduced to the St. Clair and Detroit Rivers in 1982-1983 showed highest OCS levels (55 ng/g) after residence near Sarnia; slightly less contamination was found in the clams placed a short distance downstream (22 ng/g) and at Port Lambton, at the mouth of the river (29 ng/g). OCS was detected in over 70 percent of clams transferred into the Detroit River.

Pugsley et al. (1985) quantified OCS levels in native clams along the Huron-Erie corridor and found relatively high concentrations in clams of Lake St. Clair (43.3 ng/g) but concluded that no determinations could be made regarding the distribution or levels of contaminants in these species north of Lake St. Clair due to the scarcity of clams in the St. Clair River. OCS levels in Detroit River clams (48.7 ng/g) were comparable to those of clams in Lake St. Clair.

Ciborowski & Corkum (1988) quantified the OCS contamination in aquatic insects along the St. Clair and Detroit Rivers in July 1986. They reported significantly higher OCS concentrations in insects from the St. Clair River, compared to insects from the Detroit River. Spatial distributions of OCS concentrations in insects on the St. Clair River were significant. For caddisflies, OCS levels averaged 415.4 ng/g and 147.2 ng/g for the Sarnia and Port Lambton areas, respectively.

In 1985-1986, yellow perch, spottail shiners, and emerald shiners were caught from the shores of the St. Clair and Detroit Rivers by Suns and Hitchin (1992). The average concentration in fish from the St. Clair River at Lambton Generating Station, midway between Sarnia and Lake St. Clair, was 84.8 ng/g. By contrast, fish from the South Channel, in the St. Clair River delta, averaged 43 ng/g OCS, and only 3-5 ng/g OCS was reported for fish caught at the mouth of the Detroit River (Suns and Hitchin 1992).

Hebert et al. (1990) reported similar concentrations in the livers of non-migratory mallards (115.3 ng/g) and non-migratory redheads (85.6 ng/g) collected from the St. Clair River delta in 1986. For comparison, OCS levels in the livers of migratory mallards (56.1 ng/g) and migratory redheads (18.9 ng/g) were also quantified. Significantly higher OCS concentrations in resident ducks of the St. Clair River delta indicated higher exposures to OCS in this area.

Ashtabula River

Ashtabula, Ohio, lies on the southern shore of Lake Erie. This area is the site of reported OCS-contaminated fish and several industrial processes using chlorine (Kuehl et al. 1981). The highest OCS concentration identified from a bank of Great Lakes fish was 405 ng/g in a 1979 sample taken from the Ashtabula River at Ashtabula, Ohio. A composite fish sample consisting of several fish species collected from the Ashtabula River in 1976 revealed a level of 144 ng/g OCS, and the OCS content of a similar sample from 1978 was 152 ng/g. Concentrations of 256 ng/g and 184 ng/g, respectively, were also quantified in 1979 and 1980 fish samples from Fields Brook in Ashtabula, Ohio.

Lake Ontario

Reports indicate that the earliest OCS contamination of Lake Ontario was discovered in 1976. However, the OCS concentration of 11 dated sediment samples from various locations in Lake Ontario indicated that OCS contamination of the lake began about 1940 (Kaminsky & Hites 1984). From these samples, the contamination was shown to reflect chlorine production patterns in the Great Lakes area. "Taffy tar" generated by the use of graphite anodes in the production of chlorine was considered the source of OCS contamination in Lake Ontario. A sharp drop in OCS concentrations after 1970 was correlated with an industry-wide shift to metal anodes (Kaminsky & Hites 1984). Further, these authors attributed the OCS at each of nine contaminated sites identified in the United States to the presence of a chlorine producer who used graphite anodes prior to 1970. The absence of OCS contamination in other areas not containing a chlorine producer (e.g. Lake Superior and Lake Michigan) confirmed their hypothesis that the primary source of OCS in the Great Lakes was taffy tar from chlorine production, most notably from the four major chlorine manufacturers on the Niagara River.

Although OCS has since been identified at several locations in and around Lake Ontario, investigations into contamination along the Niagara River continued to indicate significant inputs of OCS emanating from this area. In 1984, Jaffe and Hites (1986) analyzed the OCS levels in non-migratory fish from the Niagara River and Lake Ontario tributaries. Considerable OCS

contamination was detected in tributaries along the southern shore of Lake Ontario at Sodus Bay (310 ng/g), Salmon River (140 ng/g), and Oak Orchard Creek (210 ng/g). The highest OCS concentrations were measured in carp at locations immediately downstream of Hyde Park dump: 18 Mile Creek (900 ng/g), Fort Niagara (410 ng/g), and 12 Mile Creek (340 ng/g). High concentrations along the Niagara River were also found at Bergholtz Creek (650 ng/g) in the Love Canal area.

By comparison, the OCS level in non-migratory fish at the mouth of the Oswego River in eastern Lake Ontario was reported to be 35 ng/g by Jaffe and Hites in 1984. This level is approximately the same as that reported six years earlier by Kuehl et al. (1981), indicating no local sources of OCS. However, north of Oswego in Lake Ontario, the OCS content of fish from Cape Vincent, New York, was reported to be 281 ng/g in 1977 (Kuehl et al. 1981). Huestis et al. (1996) also reported an elevated level of OCS (263 ng/g) in 1977 in fish north of Main Duck Island in the eastern basin of Lake Ontario. Even higher OCS levels (480 ng/g) were detected in fish upstream at St. Lawrence (Jaffe and Hites 1986).

Compared to fish caught in tributaries of the Niagara River and Lake Ontario, fish from collection sites on the Niagara River or in Lake Ontario show lower levels of OCS contamination. Suns and Hitchin (1992) reported OCS (4.5 ng/g) in fish at Search and Rescue, New York, on the Niagara River in 1982, but could not detect OCS in fish at Oakville Harbour of Lake Ontario in 1987. In 1981 Suns et al. (1983) reported similar OCS levels of 3 ng/g in fish from the Niagara River at Lewiston and Peggy's Eddy, New York, and at Niagara-on-the-Lake, Ontario.

Lake Ontario sediments contain nearly the same level of OCS contamination as fish in the Niagara River, as found in samples collected near the Niagara River in 1981. Fish levels of 4.3 ng/g and suspended sediment levels of 4.0 ng/g were similar from the eastern, middle, and western basins of Lake Ontario (Durham & Oliver 1983, Oliver & Niimi 1988). When samples from the Kingston Basin (inlet to the St. Lawrence River) are included in the mean concentration of bottom sediments collected from Lake Ontario, the level of OCS contamination averages 11 ng/g (Oliver & Niimi 1988).

Lake Superior

OCS was not detected in fish samples collected from Apostle Islands, Wisconsin, on the western end of Lake Superior in 1974, nor in samples from Copper Harbor, Michigan, at the point of Keweenaw Peninsula in the middle of Lake Superior in 1980 (Kuehl et al. 1981). Jaffe et al. (1985), however, discovered OCS (6.8 ng/g) in localized fish of Keweenaw Bay in 1983, though not in fish of three tributaries feeding Lake Superior from upper Michigan. In eastern Lake Superior, OCS levels in fish of the Upper St. Marys River were as high as 205 ng/g in 1983, though OCS could not be detected in fish from the Lower St. Marys River or Tahquamenon River (Jaffe et al. 1985).

Siskiwit Lake, a remote lake on Isle Royale in Lake Superior, receives no inflow from Lake Superior and is far from potential point sources. The presence of OCS in Siskiwit Lake lake trout and whitefish (17.7 ng/g) implies atmospheric transport of this contaminant from remote sources (Swackhammer and Hites 1988).

Lake Michigan

Data on OCS levels in Lake Michigan are limited, presumably due to the low level of contamination in this lake. Kuehl et al. (1981) report that the OCS content of fish from Lake Michigan was less than 5 ng/g.

3.3 OCS IN OTHER WATERS

The following discussion addresses locations both nationally and internationally where OCS has been detected in environmental media. The data are, for the most part, episodic in nature, having been collected in relatively small geographic regions over relatively short periods of time. Because of the episodic nature of these data, it is difficult to draw definitive conclusions about temporal and spatial distributions.

Bayou d'Inde, Louisiana

Nearly 400 sites across the U.S. were analyzed for chemical contamination of fish between 1986 and 1989, as reported in *A National Study of Chemical Residues in Fish* (Kuehl and Butterworth 1994). Thirty-six of the 400 sites contained OCS-contaminated fish, at an average concentration of 1.7 ng/g. High concentrations of OCS were measured in fish from Corpus Christi Harbor, Texas; the Hylebox Waterway, Tacoma, Washington; and Jamaica Bay (mouth of Hudson River), New York. The highest concentration of OCS recorded in this study (138 ng/g) was found in catfish at Bayou d'Inde, Sulfur, Louisiana.

The Bayou d'Inde area contains chemical, petrochemical and agrochemical industries that manufacture or process petroleum, sodium hydroxide, chlorine, Teflon®, butadiene, synthetic rubber, trichloroethylene, and perchloroethylene. Effluents from these industries are discharged into Bayou d'Inde. Catfish collected near an industrial outfall of Bayou d'Inde had OCS levels of 2100 ng/g; bottom sediments and suspended sediments near this outfall contained 56,000 and 5,600 ng/g of OCS, respectively. OCS was not detected in water near the industrial outfall. Farther downstream at the junction with the Calcasieu River, the OCS concentration in catfish was 300 ng/g, and in blue crabs 1000 ng/g. OCS was not detected in catfish approximately 5 miles away in Lake Charles (Pereira et al. 1988). Despite the similarity of locations and time of this study with respect to the one above, there were, clearly, major differences in the levels of OCS detected.

St. Lawrence River

Freshwater mussels from the St. Lawrence River between Lake Ontario and Trois Rivières and from the Ottawa River were collected and analyzed for organic industrial contaminants and pesticides in 1985 (Metcalf and Charlton 1990). OCS was identified as a minor organic contaminant and detected in the St. Lawrence River mussel samples only. Its presence in St. Lawrence River mussels was purportedly due to transported contaminated sediment from Lake Ontario.

Gulf of Mexico

Bottlenose dolphins along the Texas coast and in the Gulf of Mexico were found to be contaminated with OCS in 1990, whereas dolphins from the Alabama and Atlantic coasts were not (Kuehl and Haebler 1995). Interestingly, the mean concentration in immature dolphins from the Texas coast was much greater (244 ng/g) than the mean concentration in male (30 ng/g) or female (28 ng/g) adult dolphins from the same area. The reason immature dolphins had such high concentrations of OCS was not known.

North Sea

Organochlorine levels in North Sea sediments were investigated by Lohse (1988). Sediment samples collected between December 1994 and May 1987 from an international combustion area in the southern North Sea were found to contain exceptionally high concentrations of OCS. Since 1982, Atlantic cod of the North Sea have been analyzed for OCS (de Boer 1989). In 1989, mean concentrations of OCS in cod were reported for the northern North Sea (4.1 ng/g), central North Sea (7.8 ng/g), and southern North Sea (45 ng/g), depicting an increasing trend from the northern to southern North Sea, where ocean incineration previously occurred.

Concentrations of OCS in marine organisms in the incineration area of the North Sea were measured in 1988-1990 (Dethlefsen et al. 1996). Significantly higher concentrations of OCS were consistently found in fish and invertebrate species from this area, as compared to reference areas. As noted by Dethlefsen et al., "Fishes of the North Atlantic do not normally contain OCS (Ernst *et al.* 1984; Luckas and Harms 1987), however, this substance has been repeatedly detected in organisms from the North Sea." Organochlorine wastes were burned on ships in the incineration area, northwest of the Dutch coast, until the practice was stopped in 1991. The authors presume that OCS was formed during the incineration process and then released with the unfiltered combustion residues into the atmosphere of the open sea. With wet and dry deposition, OCS was introduced into the water of the North Sea and accumulated in marine organisms.

Elbe Estuary

In Germany, sediments collected between Hamburg and Cuxhaven along the Elbe River in 1983 were analyzed and reported to contain OCS levels of 0.52-5.5 ng/g (Eder et al. 1987). The Elbe estuary near Hamburg was again investigated in 1985-1987 by Krieg and Kausch

(1993). Sediment contamination was shown to be as high as 225 ng/g of OCS in the inner harbor of the Elbe and 59-79 ng/g of OCS in erosional zones of the Elbe channel. The pollutant content in worms collected in these areas indicate that these organisms also accumulate the contaminants found in the sediment (Kreig and Kausch 1993).

Norwegian Coasts

In Norway, the area surrounding the magnesium-producing plant where OCS was first discovered was revisited in 1975-1976 (Ofstad et al. 1978). Certain species of fish (cod, whiting, and pollack) were found to contain unusually high levels of OCS. The highest concentration of OCS was identified in cod liver (431,000 ng/g) from the Frierfjord; concentrations in other species varied from 5,800 ng/g in eel to 67,000 ng/g in whiting (144,000 ng/g in whiting liver).

In 1987-1988, the contamination of Frierfjord by the magnesium-producing plant was once again studied. Knutzen and Oehme (1989) reported that a change from coal to coke in the production process reduced the load of OCS in the plant effluent by about 90 percent in 1975-1976. They further stated that this improvement caused a subsequent decrease in OCS levels in fish (cod liver) from the Frierfjord within a year and that concentrations have persisted at these levels.

Other areas of Norway were investigated in a study of herring gull eggs from seven different locations along the coast in 1979-1981 (Moksnes and Norheim 1986). OCS was found in just one location, Telemark, where the level there (140 ng/g) was attributed to a local discharge of the chemical.

River Rhine

Eels caught in the river Rhine delta of The Netherlands in 1981 were the subject of an eight-year study of the elimination of organochlorine compounds under natural conditions (de Boer et al., 1994). The concentration of OCS in the eels, prior to commencement of the elimination study, was 650 ng/g wet weight.

3.4 TIME TRENDS

The lack of consistent, ongoing monitoring efforts aimed at OCS and the paucity of data regarding current OCS levels limit the determination of time trends in the Great Lakes and elsewhere. The few conclusions that can be drawn are limited to studies that tracked OCS concentrations at specific historically contaminated sites.

In the Great Lakes, Kaminsky and Hites (1984) found a correlation between OCS levels in Lake Ontario sediments and the production of chlorine in the Great Lakes area. Their analysis of sediment cores from Lake Ontario suggested that OCS concentrations rose with the onset of chlorine production and growth of the industry, and then fell with the conversion from graphite to metal anodes within the industry. A rapid decline in OCS levels coincided with the

conversion to metal anodes in the 1970s because graphite anodes were thought to produce the waste mixture known as “taffy tar”. The newer metal anodes do not generate such waste. Similar graphite-anode technology in the production of magnesium could also have contributed to the OCS concentrations observed in Lake Ontario sediments. The magnesium industry in the Great Lakes is limited to one major producer; the chlorine industry is comprised of several major chlorine manufacturers in the Great Lakes area (Kaminsky and Hites 1984).

Durham & Oliver (1983) similarly uncovered the history of chlorinated hydrocarbon contamination buried in Lake Ontario sediments and related this historical record to U.S. production of chlorobenzenes for corresponding years. OCS concentrations in Lake Ontario sediments from ~1900-1980 are shown in Figure 2. The OCS-contaminated sediments, obtained at the mouth of the Niagara River, reveal that peak contamination of the river occurred around 1960, coinciding with the peak period of chlorobenzene production in the U.S. from 1960 to 1970.

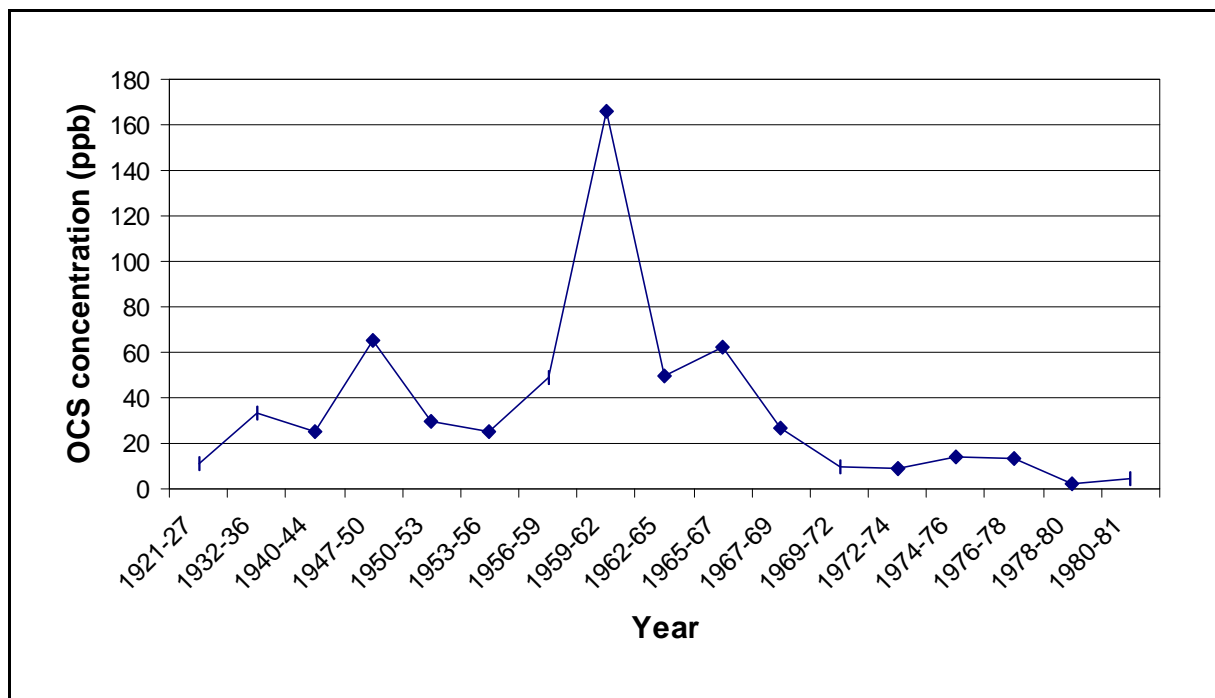


Figure 2. History of OCS Contamination in Lake Ontario Sediments.

More recently, Huestis et al. (1996) tracked OCS levels in lake trout from Main Duck Island in eastern Lake Ontario. Figure 3 shows a general decreasing concentration of OCS in Lake Ontario trout from 263 ng/g in 1977 to 31.3 ng/g in 1993. Although OCS concentrations in Lake Ontario trout decreased 88 percent over the 16 year period, fairly steady concentrations were observed from 1986 to 1993. The mean concentration for this period is 35 ng/g.

Elsewhere in the Great Lakes area, Chan (1993) reported 26.9 ng/g and 15.2 ng/g OCS in sediments collected at the mouth of the St. Clair River in 1988 and 1989, respectively, a 42 percent decline. However, Drouillard et al. (1996) report recent OCS levels in Detroit River sediments (23.9 ng/g) that are similar, if not higher than, those reported in 1985 (Pugsley et al. 1985, Oliver and Bourbonniere 1985). The OCS content of insects exposed to these sediments (48.7 ng/g) is likewise comparable to OCS concentrations in insects from the Detroit River collected in 1986 (Ciboroski and Corkum 1988). Historical data from studies show some conflicting trends in the concentrations of OCS in sediment which cannot be resolved at this time. Recent studies showing OCS levels have not declined may indicate local sources.

A decreasing time trend has been shown for OCS levels in the southern North Sea from 210 to 33 ng/g between 1977 and 1987 (de Boer 1989). Slight decreases in the central and northern North Sea areas have also been determined from the first detection of OCS in 1983 until 1987.

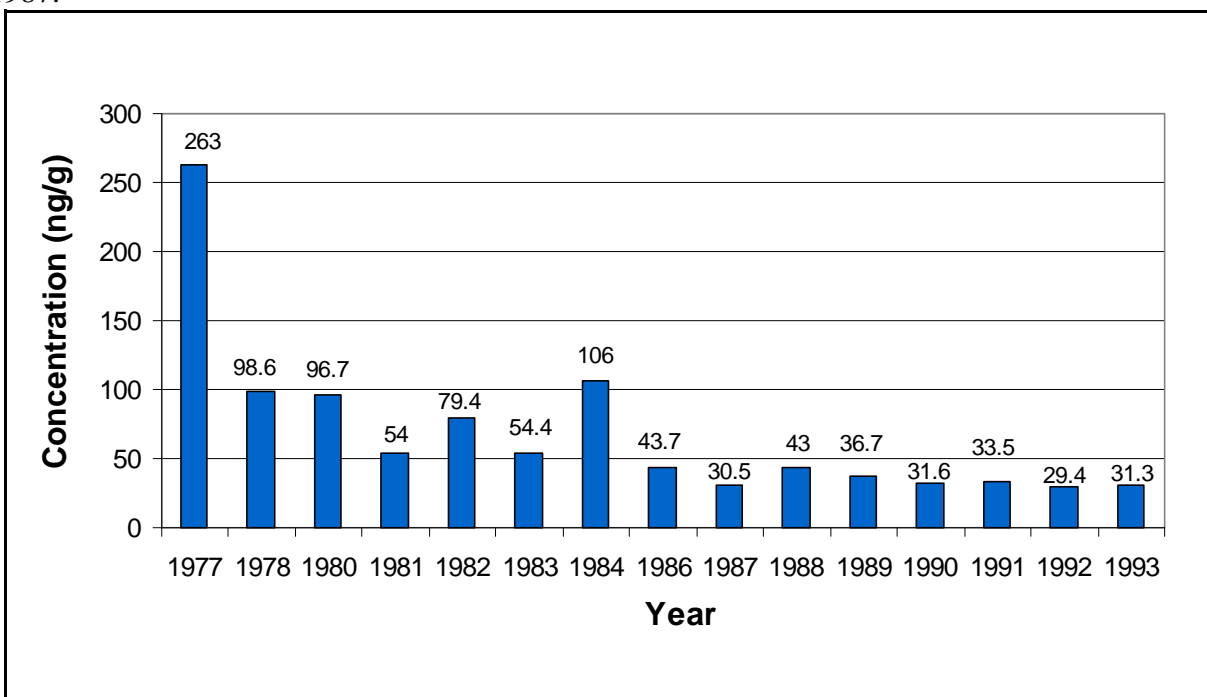


Figure 3. Concentrations in OCS in Lake Ontario Trout, 1977-1992.

The concentrations of OCS in herring gull eggs collected from Telemark, Norway, in 1979-1981, compared with those of eggs collected from the same location in 1969, reveal a significant decrease in OCS levels over the decade (Moksnes & Norheim 1986). However, such a decrease was not observed in herring gull eggs elsewhere in the country.

3.5 BODY BURDENS

Measurements of OCS in human tissues is limited. Most recently, Health Canada has published *Persistent Environmental Contaminants and the Great Lakes Basin Population: An Exposure Assessment* (1998). In the chapter on OCS, Health Canada estimates the total exposure to OCS for Great Lakes Basin residents to be 0.02 ng/kg body weight per day (ng/kg bw/day) for adults aged 20 and older and 12.86 ng/kg bw/day for breast-fed infants less than six months of age. For adults who consume Great Lakes sport fish, total exposure to OCS is estimated at 0.45 ng/kg bw/day. The Minimum Risk Intake (MRI) for OCS from food, set by the Food Directorate of Health Canada, is 310 ng/kg bw/day.

Health Canada's OCS exposure assessment includes intake routes from ambient and indoor air, soil and house dust, drinking water and food. Numerous assumptions were made because no data exist for OCS levels in indoor air or house dust and data on food consumption is limited to intake of freshwater fish from the Great Lakes. Since more than 96 percent of exposure is thought to be derived from food supplies, the daily intake estimates are probably conservative. Exposure to OCS from Great Lakes fish is of particular concern for mothers who breast feed. Accumulation of OCS in a mother's breast milk, and subsequent consumption by her nursing infant as almost the sole source of nutrition, results in significant exposure for infants under six months of age.

A 1986 investigation of chlorinated hydrocarbon residues in the breast milk of Canadian women reported a mean OCS concentration of 5.2 ng/g in milk fat and a maximum value of 191.5 ng/g in milk fat (Mes et al. 1993). The median level of OCS in the breast milk of women in the Province of Ontario was 0.12 ng/g (whole milk), whereas the median levels in all other Canadian provinces were below the minimum detectable level. No relationship was found between the amount and type of fish eaten and chlorinated hydrocarbon levels in the breast milk of study participants. Nor was a relationship found between maternal age and contaminant levels, although levels of certain contaminants were observed to decrease as the number of children breast-fed increased.

Relevant factors in a 1983 study of OCS concentrations in the blood of 135 residents of the Elbe estuary in Germany were age, fish consumption, place of residence, and consumption of Elbe eels (Lommel et al. 1992). OCS was detected in the blood of 40% of study participants, with levels ranging from non-detect to 9.2 ng/ml. Concentrations of 3.0 ng/ml or greater were reported in 26 of the participants. Compared to people living farther from Hamburg, people reporting their place of residence near Hamburg (especially the Kollmar area) were more frequently found to have significantly higher concentrations of OCS in their blood. The same was true for residents who often ate fish (more than 0.3 kg/week) or Elbe eel. However, people who lived in areas of high contamination, such as Kollmar, but rarely ate fish were also more often contaminated with OCS. The study suggested that other regional factors (for example, municipal waste incineration) must have an effect. Body burdens were also shown to increase with age in the study of Elbe River residents. While the median concentration of OCS in the blood of participants aged 50 or under was not detectable, the median concentration for participants 61 or older was approximately 2.4 ng/ml.

4.0 POTENTIAL PAST OR PRESENT SOURCES

4.1 MECHANISMS OF FORMATION OF OCS

Laboratory synthesis reactions and process testing suggest that production of OCS can occur by one of several routes: addition reactions between chlorinated species, chlorination of alkane/alkene compounds, and chlorination of elemental carbon. In the latter case, it appears that OCS is formed under electro- and thermo-chemical conditions whenever a carbon source is exposed to chlorine and a large energy flux (electricity or heat). This *de novo* synthesis reaction, i.e., the formation of complex aromatic species from elemental carbon and chlorine, has been examined extensively as a mechanism for formation of chlorinated dioxins and furans (Gullett, 1998).

Chlorination of carbon can produce many of the smallest precursor chlorinated alkanes and alkenes that are required as building blocks for OCS. This reaction has been shown using as the substrate elemental carbon, soot, graphite, and fly ash. The chlorine for this reaction is also ubiquitous. Chlorine occurs naturally in all fossil fuels- wood, oil, coal, etc. Chlorine is also present in waste incineration processes in the form of chlorinated polymers such as PVC.

Blackwood and Cullis (as examined in Schulman and Klingele, 1985) showed that chlorination of elemental carbon at 600-800 °C and moderate pressure produced carbon tetrachloride (CCl_4), tetrachloroethylene (perchloroethylene, C_2Cl_4), and hexachloroethane (perchloroethane, C_2Cl_6). OCS has been formed via the chlorination of alkanes and alkenes. For example, the chlorination of propylene (C_3H_8) produced primarily carbon tetrachloride (CCl_4) and tetrachloroethylene (C_2Cl_4), and smaller amounts of perchloroethane, perchlorobutadiene, perchlorobenzene (HCB, hexachlorobenzene), and OCS (CA: 95(20) 225086; as reviewed in Schulman and Klingele, 1985). Lauterbach (as reviewed in Schulman and Klingele, 1985) demonstrated formation of hexachlorobenzene (HCB) from reactions between carbon and atomic chlorine. Chlorination of fly ash produced HCB, decachlorobiphenyl, and OCS. The data from these reactions do not overlap completely in the detection of all species, but it is probable that all species from carbon tetrachloride up to OCS and higher were formed in all reactions. *In toto*, these data provide the foundation for linking elemental carbon with formation of OCS.

This *de novo* synthesis mechanism is shown schematically in Figure 4 and is much simplified relative to true combustion conditions. The effects of sulfur and heavy metals (that may act as catalysts) are not included here. Stepwise condensation and/or addition reactions that involve highly chlorinated alkenes, such as tetrachloroethylene, build molecules of increasing molecular weight with a resonance-stabilized diene structure. As shown in Figure 4, the OCS reaction pathway is thought to involve, initially, the production of carbon tetrachloride and the trichloromethane radical (I and II). Reaction of two trichloromethane radicals will produce hexachloroethane, which will undergo dechlorination to tetrachloroethylene (II). Subsequent chlorine radical addition to tetrachloroethylene, condensation of two radical species, followed by elimination of molecular chlorine gives hexachlorobutadiene, C_4Cl_6 (III). Chlorine radical addition to both hexachlorobutadiene and tetrachloroethylene provides the two radicals that can

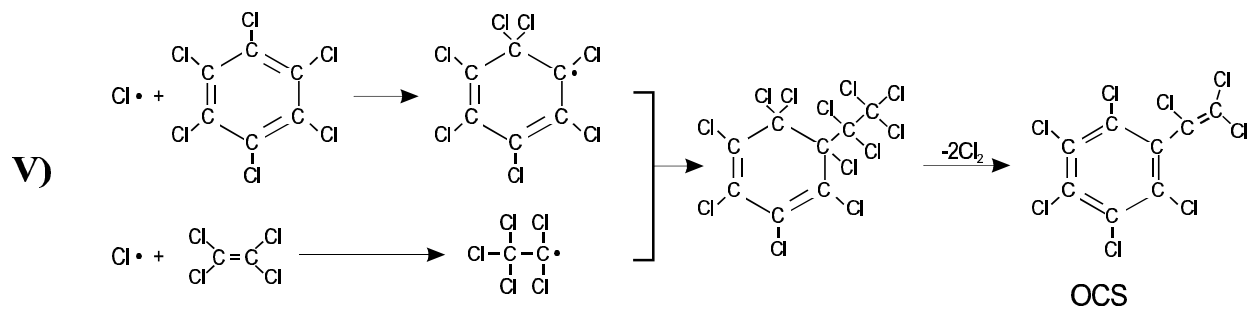
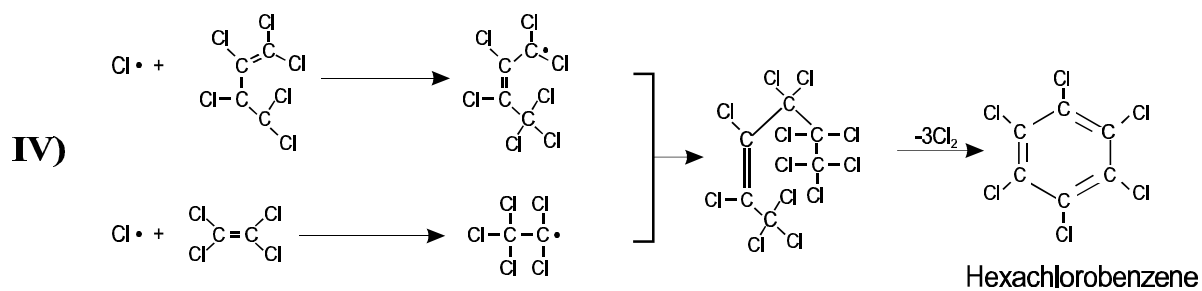
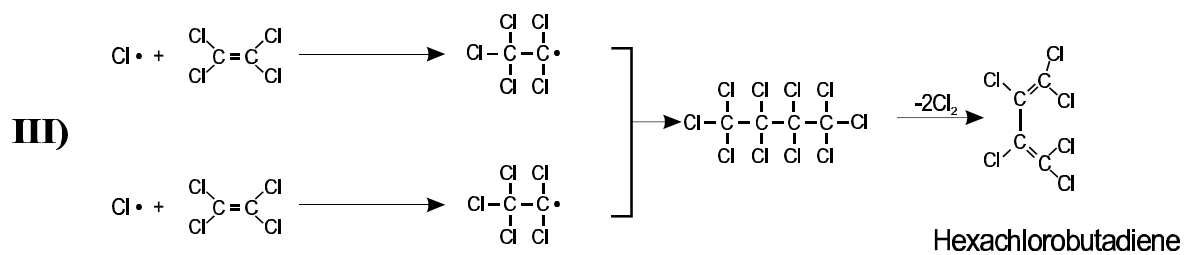
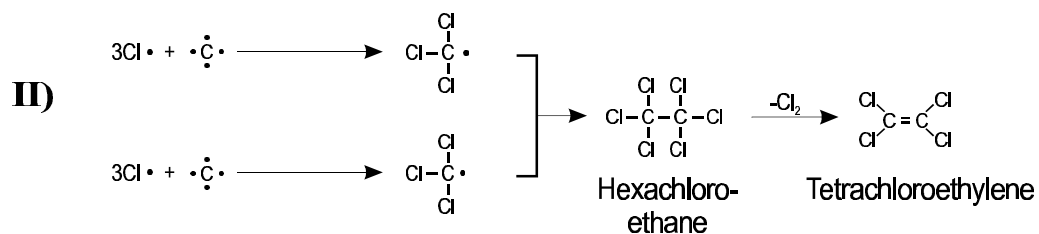
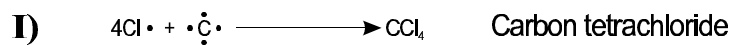
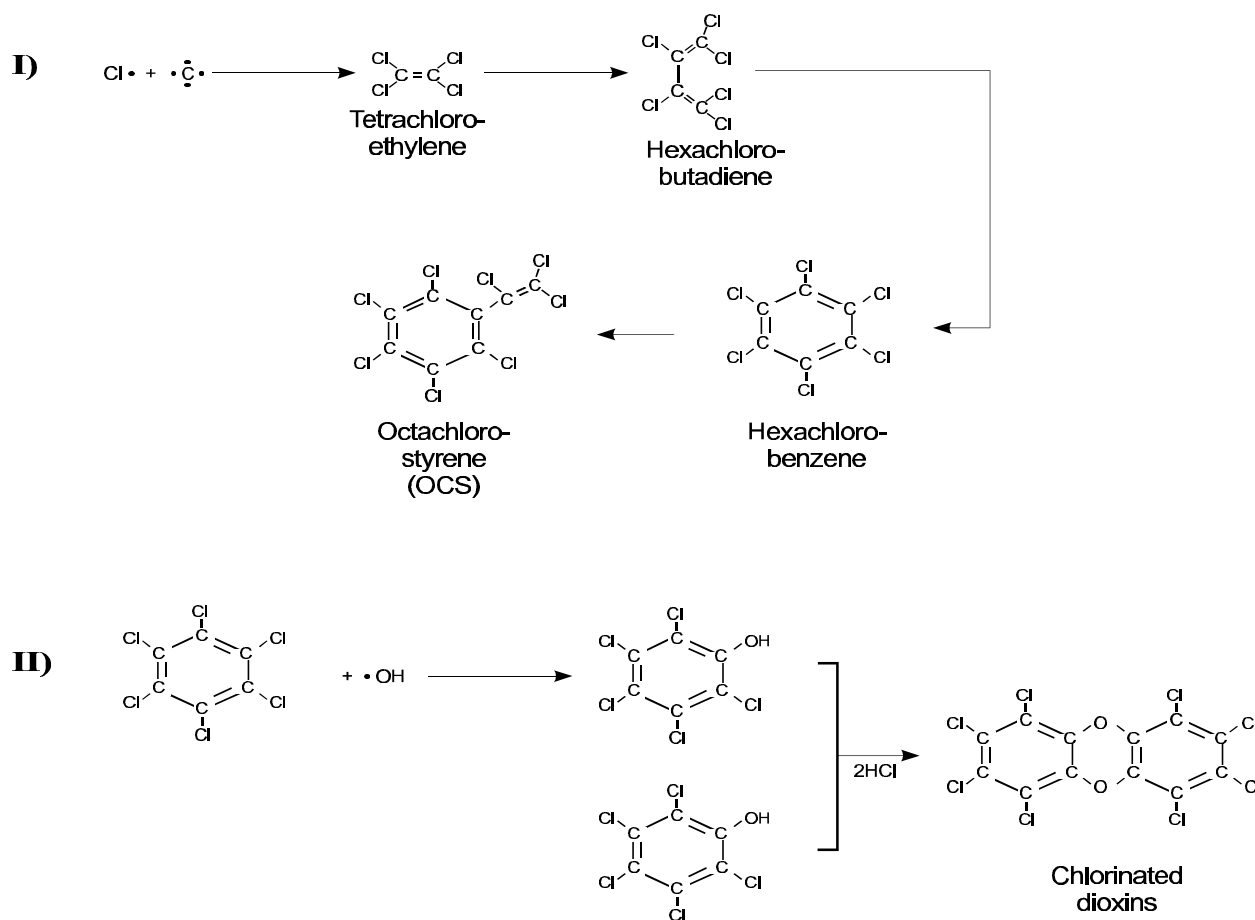


Figure 4. *De novo* Synthesis of OCS

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Chlorination of aromatic species has also been shown as a pathway for production of OCS: OCS, rather than perchloro ethylbenzene, was formed in high yield (85%) from the chlorination of ethyl benzene (Rvetman, 1973; as reviewed in Schuyman and Klingele, 1985). In between these two extremes, chlorination of carbon and chlorination of aromatic compounds, are the production methods that rely on condensation reactions between relatively small chlorinated compounds, such as tetrachloroethylene.

Any incineration or combustion process will have, in addition to chlorine radicals, highly



reactive hydroxy radicals (OH^\cdot). Hydroxy radicals will also be present during high temperature reactions with carbon-based electrodes where oxygen is present. The addition of the hydroxy radicals to the combustion conditions leads to the formation of chlorinated phenols that are completely analogous to chlorinated benzenes, with substitution of an OH group for one of the chlorines. Chemical reaction between two chlorinated phenols leads to production of chlorinated dibenzodioxins (chlorinated dioxins) and chlorinated dibenzofurans (chlorinated furans).

This reaction for production of chlorinated dioxins is included in Figure 5. For this reason, whenever chlorinated dioxins and furans are detected, it is probable that OCS and HCB are present, and conversely, whenever HCB and OCS are detected, chlorinated dioxins are probably also present. The relationship between emissions of HCB, OCS and chlorinated dioxins has been discussed in numerous reports.

Because of the similarity of mechanisms for the formation of HCB, chlorinated dioxins and OCS, the emission inventories for HCB and dioxin may be used in a most simplistic manner to estimate the amounts of OCS that may be formed and/or released. This type of calculation may be carried out for only the most preliminary estimate of OCS levels, to be used in assessments of whether OCS reporting needs to be continued. It is not intended to replace the formal emissions inventory testing and reporting procedures, but to serve as a guide in the absence of more concrete data at this time.

The average ratio of OCS to HCB in sediment may be used to estimate the loadings of OCS emitted. The assumptions here are that OCS and HCB are formed in approximately the same ratio in all emitting industries (Oehme et al., 1989), and in that same ratio are also discharged to water, and accumulate in the sediment near an industrial outfall. Since continuous replenishment of the chemicals is assumed for an outfall area, and water solubility for both compounds is very low, the ratio of the two compounds in the sediment of an outfall area may more likely represent the source profile than the competing effects of degradation, migration and/or uptake.

Similarly, the ratio of dioxin to OCS in sediment would be a desirable ratio to discern for the purposes of using the dioxin emissions inventory to predict potential OCS levels being emitted (Oehme et al., 1989). Unfortunately, analyses of dioxins and OCS from the same sediments has not been carried out and/or reported, and thus the calculation of OCS to dioxin at a source is more speculative than the calculation of OCS to HCB at a source. Due to this fact, we have extrapolated from the sediment model described above, and used data reported on levels of OCS and dioxins in fish for calculations. We have assumed that OCS and dioxins move in the same direction in the biosphere with respect to partitioning, bioconcentration and bioaccumulation, and that the levels of these two compounds in fish occur via the same pathways of uptake. The concentration difference between dioxins and OCS in the same fish should reflect the original ratio from the emitting source, multiplied by the relative difference in bioaccumulation. Bioaccumulation factors for 2,3,7,8-octachlorodibenzodioxin and OCS differ by a factor of approximately a factor of 10, with OCS accumulating at a 10-fold greater rate (USEPA, 1995).

With this framework in mind, and the availability of data from HCB and dioxin emissions inventories on numerous emission sources, the following sources have been classified with respect to OCS emission as either documented, highly probable, or suspected.

4.3 SUMMARY OF SOURCES OF OCS

A comprehensive emissions inventory of source categories of OCS has never been undertaken. Emissions test data are extremely limited. Emissions of OCS from a few industrial processes carried out under simulated laboratory conditions have been quantified, but the majority of evidence indicating sources of OCS comes from reported measurements of OCS in the environment, the conditions found to favor the formation of OCS, and the tendency for OCS to form in some of the same processes that generate HCB or dioxin.

From this evidence, several industrial processes have been identified as potential sources of OCS. The potential OCS sources can be divided into three categories, depending on their relative likelihood to release OCS. Based on recorded measurements of OCS in industrial effluents, leachates, wastes, and sediments, there are **documented** industrial processes which generate OCS as a byproduct. Industries with a **high probability** of releasing OCS have been identified on the basis of evidence that points toward the formation of OCS as a byproduct in processes involving aromatic compounds with chloroalkyl radicals or processes involving carbon and chlorine at high temperature and/or with a large flux of electrical current (Schulman and Klingele 1985). Various references in the published literature have indicated other **suspected** sources of OCS, these based largely on the similarity between the mechanisms of formation of OCS, HCB, and dioxin. Table 2 lists the documented, highly probable, and suspected sources of OCS.

Table 2. Potential Sources of OCS

Industry	Industrial Process
<i>Documented Sources</i>	
Chlor-alkali/chlorine production	Electrolytic manufacture of chlorine, sodium, potassium hydroxide, and sodium hydroxide; graphite electrodes used prior to 1970, metal anodes used subsequently
Chlorinated Solvents/Chlorobenzenes Production	High-temperature chlorination to produce carbon tetrachloride (CCl ₄) & tetrachloroethylene (C ₂ Cl ₄)
Landfill Disposal	Disposal of spent graphite electrodes into landfills; disposal of sludges from electrolysis reactions & organic solvent production; disposal of incineration ash
Magnesium production	Electrolysis of MgCl ₂ using graphite electrodes to produce Mg metal; chlorination of raw materials to produce MgCl ₂ feed
Metals Degreasing/Degassing	Use of chlorinated solvents to remove impurities (e.g. carbon deposits) from metal parts

Table 2. Potential Sources of OCS (Continued)

Industry	Industrial Process
Nonferrous Metal Smelting/Refining	
- Nickel	Extraction & refining processes utilizing chlorine
- Niobium and Tantalum	Extraction of metallic niobium by bubbling chlorine gas through niobium/tantalum ores at high temperature
- Primary Copper Smelting	Chlorinating roasting process
- Secondary Aluminum Smelting	Vaporization of chlorinated organic coatings in used beverage containers; use of chlorine in demagging
- Secondary Copper Smelting	Coke (source of carbon) combined with chlorine-containing telephone & plastic scrap in smelting furnace
- Secondary Lead Smelting	Coke (source of carbon) combined with PVC separator (formerly used in lead-acid batteries) in smelting furnace
- Titanium	Chlorination of titanium ore or chlorine regeneration from $MgCl_2$
- Vanadium	Chlorinating roasting process
Semiconductor	Aluminum Plasma Etching
Highly Probable Sources	
Ethylene Dichloride/Vinyl Chloride Production	Free-radical pyrolysis of ethylene dichloride to yield vinyl chloride
Incineration Processes	
- Boilers/Industrial Furnaces Burning Hazardous Waste	Incineration of chlorinated organic hazardous waste
- Carbon Reactivation Furnaces	Desorption of chlorinated compounds from spent carbon in reactivation furnaces
- Cement Kilns (Co-fired w/ Hazardous Waste)	Incineration of hazardous waste, especially chlorinated solvents
- Drum and Barrel Reclamation Furnaces	Incineration of chlorinated organic residues and coatings in drums
- Hazardous Waste Incineration	Incineration of hazardous wastes, especially chlorinated solvents
- Medical Waste/Pathological Incineration	Incineration of PVC & chlorinated organic waste
- Municipal Waste Incineration	Incineration of PVC (source of chlorine) & other packaging materials (carbon source); combustion of HCB in fly ash
- Petroleum Refining Catalyst Regeneration	High-temperature recovery & reactivation of spent metal catalysts with chlorine or chlorinated compounds
- Scrap Electric Wire Recovery	Incineration of PVC wire insulation to reclaim wire
- Sewage Sludge Incineration	Incineration of organic waste containing chlorine

Table 2. Potential Sources of OCS (Continued)

Industry	Industrial Process
- Uncontrolled Combustion of PCBs	Accidental or intentional burning of PCBs
PVC Polymerization/Production	Free-radical initiated vinyl chloride polymerization
<i>Suspected Sources</i>	
Bleached Chemical Wood Pulp & Paper Mills	Use of chlorine and chlorine dioxide to bleach wood pulp (source of carbon)
Cement Kilns(Non-Hazardous Waste Burning)	
Coke Production	Heating & distillation of coal containing chlorine; treatment of coal with chlorine at high temperatures
Fuel Combustion	
- Coal Combustion	Combustion of coal containing chlorine in utility and industrial boilers
- Oil Combustion	Combustion of residual oils containing chlorine
- Vehicle Fuel Combustion	Incomplete combustion of fuel or oil additives (e.g., dichloroethane, pentachlorophenolate)
- Wood Combustion	Combustion of PVC-coated wood, preservative-treated wood, etc.
Kraft Recovery Boilers	Combustion of black liquor containing chlorides to recover beneficial chemicals
Landfill Fires	Accidental combustion of chlorinated organic waste (e.g., rubber, plastic, PVC)
Pesticides Manufacture	
- Mono- to Tetrachlorophenol Production	Thermal or chemical breakdown of chlorophenols
Pentachlorophenol Production for Wood Preservation	Thermal or chemical breakdown of chlorophenols
Primary Aluminum	Electrolytic purification or manufacture of aluminum using a chloride salt and graphite electrodes
Pulp & Paper Mill Sludge Incineration	Incineration of mainly wood residues along with sludge containing chlorides
Synthetic Graphite Production	Pyrolysis of petroleum and coke at high temperatures
Tire Manufacturing	High-temperature processes involving chlorine compounds

Table 2. Potential Sources of OCS (Continued)

4.4 CHLOR-ALKALI/CHLORINE PRODUCTION

Chlorine and caustic soda (sodium hydroxide) are produced concurrently in an electrolytic cell containing a chloride salt solution.¹ The passage of current through the cell liberates chlorine gas from the solution at the anode. Hydrogen gas and caustic soda are generated at the cathode in diaphragm and membrane cells. In a mercury cell, a sodium-mercury amalgam is produced at the cathode and the amalgam is removed and further reacted to form hydrogen and caustic soda. The choice of cell depends on many variables including caustic soda strength and purity requirements (Buonicore and Davis 1992). Today, chlorine from diaphragm cells accounts for 76 percent of U.S. chlorine production. Of the remaining 24 percent, more is produced using mercury cells than membrane cells, although membrane cells are typically chosen for new production facilities because of their greater efficiency and economic advantage (Kirk-Othmer 1996).

The chlorine industry has historically been associated with OCS contamination in Lake Ontario sediments due to chlorinated organic waste products generated from the industry-wide use of graphite electrodes in electrolytic cells prior to about 1970 (Kaminsky & Hites 1984). The source of this waste was chlorination of the coal tar used to bind the graphite electrodes. The release of the resulting sludge and spent graphite anodes into the environment led to the presence of OCS in all major sediment depositional areas of Lake Ontario. Kaminsky and Hites found that, of the nine locations in the U.S. where OCS was identified in fish or sediments, all nine could be associated with a nearby chlorine producer.

From inception until about 1979, graphite was used exclusively as the anode in chlorine production. In the late 1960s, chlor-alkali producers began switching to metallic anodes because of the significant energy cost savings. It is believed that nearly all chlor-alkali producers now use ruthenium oxide titanium-coated anodes, also known as dimensionally stable anodes (DSA) (Kirk-Othmer 1996). Lacking carbon, these improved anodes are not expected to generate OCS. However, a recent analysis of metal electrode sludge from a chlorine production facility, conducted as part of the Swedish Dioxin Survey, revealed high chlorinated dibenzofuran (CDF) levels similar to those reported for graphite electrode sludge (Strandell et al. 1994). In addition, the total abandonment of graphite electrodes in the chlorine industry has not been verified, and the treatment and disposal practices for spent graphite electrodes used prior to the industry-wide switch to metal electrodes are not known. Under RCRA, EPA currently regulates the land disposal of wastewater and sludges generated by chlorine production facilities that use the mercury cell or the diaphragm cell with graphite electrodes, although the regulations do not target OCS.

¹Electrolysis is the flow of current, within a cell, from the anode through the electrolyte (usually a solution) to the cathode and out of the cell. The electrolyte is consumed, and decomposition products are formed at the electrodes.

Further uncertainty regarding the potential for chlorine producers to generate OCS arises from the composition and location of membrane components used in membrane cells. In a membrane cell, the anode and cathode compartments are separated by a cation-exchange membrane. One side of the membrane is exposed to chlorine, which is released at the anode, while the other side must withstand strong caustic. Commercial membranes employed in this type of cell consist of bonded layers of a perfluorosulfonate polymer, a Teflon fabric, and a perfluorocarboxylate polymer. Trade names for commonly used membranes are DuPont's Nafion and Asahi Glass's Flemion, both of which have a high carbon content. In modern membrane cells, called zero-gap or membrane-gap electrolyzers, improved performance is achieved by eliminating the gap between the electrodes. In these cells, the carbon-containing membrane is in direct contact with the anode where chlorine is produced (Kirk-Othmer 1996). These conditions raise questions about the potential for formation of OCS.

The electrolytic decomposition of hydrochloric acid to recover chlorine gas is a commercial process in operation at Mobay Chemical Company in Baytown, Texas. The graphite electrodes used in this electrolytic cell process are operated at temperatures below 85 °C and at a cell voltage of about 1.9 V (Kirk-Othmer 1996). These conditions may or may not be sufficient to generate OCS. Since the release of chlorine at a carbon anode is the process thought to be responsible for the OCS contamination of Lake Ontario prior to the switch to DSAs, this process remains a potential source of OCS.

4.5 CHLORINATED SOLVENTS/CHLOROBENZENES PRODUCTION

Analysis of the waste products generated by the high-temperature process for commercial production of carbon tetrachloride and tetrachloroethylene showed that OCS, among other chlorinated compounds, was present (Markovec and Magee 1984). Other investigators have identified OCS as a byproduct in the chlorinolysis of propylene to produce carbon tetrachloride and tetrachloroethylene (Schulman and Klingele 1985).

The impact of a chlorinated organic solvent production facility can be seen in the recent discovery of OCS-contaminated river water and food in the surrounding farms and gardens of Flix, Spain (Otero & Grimalt 1994). In this study, OCS and other chlorinated organic compounds found in food samples were considered representative of factory emissions. Similarly, chemical plants manufacturing trichloroethylene and perchloroethylene were assumed to be the source of OCS in water, sediment, and biota near an industrial outfall in the Bayou d'Inde area of Louisiana (Pereira et al. 1988). Chemical manufacturers along the Niagara River were implicated when chlorobenzenes, chlorotoluenes, OCS, and other chlorinated compounds were quantified in Lake Ontario sediments. These chlorinated compounds were identified as either intentional products of the chemical manufacturers or waste byproducts generated in their production processes (Durham & Oliver 1983).

King and Sherbin (1986) examined the effluents of point sources in the industrial area of Sarnia, Ontario, along the upper St. Clair River and compared the chemical composition of these effluents to the components of contaminated "puddles" in the river. The point sources investigated were Dow Chemical of Canada, which manufactured caustic soda, chlorine, carbon tetrachloride, perchloroethylene, polystyrene and several other organic and inorganic products; Polysar Ltd., which manufactured ethylbenzene, styrene, and rubber latex; Esso Chemical, which manufactured PVC and polyethylene resins; Sunoco Inc., which processed crude oil into fuels and petrochemical feedstocks; the Sarnia Municipal Water Pollution Control Plant, responsible for primary treatment with phosphorus removal of municipal wastewater; and the "Township Ditch", which received the discharge and runoff from several sources prior to discharging into the St. Clair River.

Results of this study revealed OCS in the effluents of Dow Chemical and Esso Chemical and in the Township Ditch. The highest loading of OCS was found in leachate from a Dow Chemical landfill that was used to dispose of solid wastes such as chlorinated tars. Only Dow Chemical effluent contained essentially the full list of components identified in the river puddles, and these compounds were at elevated concentrations. The other point sources, with the exception of the Township Ditch, did not contain a similar fingerprint of puddle chemicals. Contamination of the Township Ditch, which empties into the St. Clair River, was thought to originate with the Dow Chemical landfill (King and Sherbin 1986).

4.6 LANDFILL DISPOSAL

The disposal of electrode waste, spent graphite electrodes, solid wastes from organic solvent production, and incineration ash into landfills could lead to leaching of OCS into the soil and groundwater runoff if the deposited wastes were known to be contaminated with OCS. The Dow Chemical landfill containing chlorinated tars, for example, had high levels of OCS measured in its leachate (King and Sherbin 1986). A landfill was the most likely means of disposal of the coal tar used to bind graphite electrodes, as well as the graphite electrodes themselves, before metal anodes were commonly used in the chlorine industry (Schulman and Klingele 1985). These wastes were surmised to be the source of OCS contaminating Lake Ontario, and their presence in landfills could be a continuing source of OCS in the environment (Kaminsky & Hites 1984). The incineration of PVC, plastics, and various chlorinated organic compounds was shown to release OCS as a byproduct of combustion (Ahling et al. 1978; Lahaniatis et al. 1989). Due to its relatively low volatility, OCS would be expected in air pollution control device dust and possibly in the ash following incineration of plastics and chlorinated organic materials. Disposal of these waste materials in landfills may lead to contaminated landfill leachates.

4.7 MAGNESIUM PRODUCTION

One of the earliest indications of a source of OCS was the report of elevated OCS blood levels in the employees of Norsk Hydro, a magnesium-production plant in Norway, compared to OCS blood levels in workers with no known occupational exposure. In 1977, the blood of 17 employees of the magnesium-production plant averaged 1.24 ng/g OCS while the blood of 9 individuals of a mercantile company averaged 0.20 ng/g OCS (Lunde & Bjorseth 1977). This magnesium production process is also assumed to be the source of OCS in fish from the Frierfjord (Ofstad et al. 1978).

Norsk Hydro operates two magnesium production plants, one at Porsgrunn, Norway, and the other at Becancour, Province of Quebec, Canada. The process used by Norsk Hydro is a two-chamber electrolytic cell which generates chlorine from magnesium chloride in the anode compartment. A source of OCS at the Norwegian plant is likely the procedure used to prepare the magnesium chloride feed for the electrolytic cell (Oehme et al. 1989). In this process, dolomite and seawater are the raw materials for small pellets composed primarily of magnesium oxide, magnesium chloride and water, with about 10 percent carbon. These pellets are fed to chlorinators to produce molten magnesium chloride. The chlorinators are cylindrical shaft furnaces which blast chlorine gas onto the pellets in the lower third of the furnaces at 1000 to 1200 °C. The molten magnesium chloride that forms in this reaction is collected at the bottom of the furnace. The suspicion of OCS formation arises from the fact that the lower third of the chlorinator furnace, where chlorine gas is introduced at high temperatures, is lined with carbon blocks that are heated by carbon electrodes.

The OCS that is almost certainly generated in these furnaces will either be among other byproduct gases, which undergo several stages of scrubbing before being released to a stack, or will adsorb to a magnesium-silicate slag that is periodically removed from the chlorinators.

The Canadian Norsk Hydro plant obtains feedstock from a different process than Norsk Hydro, Norway, and it does not appear to favor formation of OCS. However, the electrolytic production of magnesium at this plant is similar to that at Norsk Hydro, Norway, which was described as a process suspected of emitting OCS (Oehme et al. 1989). The two-chamber electrolytic cell contains graphite plates in the anode compartment. Production conditions are 700-720 °C with a current load of 350-400 kA (Kirk-Othmer 1996). The elevated temperatures, combined with chlorine on a graphite (carbon) anode, are features that strongly suggest formation of polychlorinated styrenes, including OCS (Schulman & Klingele 1985). Of additional concern is the disposal of spent graphite anode plates which may be contaminated with OCS. Typical electrolytic cells are reported to last about five years (Kirk-Othmer 1996).

Magcan, located in Aldersyde, Alberta, Canada, underwent start-up in 1990, shut down in 1991, and was still temporarily inactive in 1993. To produce magnesium metal, this facility produces magnesium chloride from magnesite ore (magnesium carbonate). The method of preparing magnesium chloride utilizes a chlorinator to react magnesite with carbon monoxide and chlorine gases. Molten magnesium chloride is collected at the bottom of the chlorinator while volatile impurities escape at the top. The construction of the chlorinator, although apparently similar to that at Norsk Hydro, Norway, has not been described. Operating temperatures are likewise unknown (Kirk-Othmer 1996). Carbon is known to be present, however, in the carbon monoxide that is fed to the chlorinator as well as in the magnesite ore. High temperatures and graphite components in the chlorinator would make this facility, if in operation, a highly probable source of OCS.

Noranda, Inc. of Toronto, Canada, uses patented technology to obtain magnesium chloride from asbestos tailings, which are magnesium silicates. This process involves reaction of the tailings at elevated temperatures with hydrochloric acid, followed by purification and drying of magnesium chloride, which is then fed to an electrolytic cell. Details of this process, including whether graphite is present in the heating process or whether graphite anodes are employed in the electrolytic cell, are not known (Kirk-Othmer 1996). However, its similarity to other magnesium production methods implies that this is a highly probable source of OCS.

Timminco of Haley, Ontario, Canada, uses the Pidgeon process in the manufacture of magnesium (Kirk-Othmer 1996). This process utilizes silicon rather than chlorine in a thermal reduction process and is not suspected of producing OCS.

Although not located within the Great Lakes Basin, the Dow Chemical magnesium plant in Freeport, Texas, and the Magcorp magnesium plant in Rowley, Utah, also have the potential to generate OCS both in the processes used to dry and purify magnesium chloride feed and in the use of graphite anodes in electrolytic cells. Long-range transport of OCS from these sources could potentially contribute to loadings in the Great Lakes.

4.8 METALS DEGASSING/DEGREASING

Aluminum Degassing

Aluminum foundries have been identified as sources of OCS. Hydrogen gas readily dissolves in molten aluminum and causes problems in aluminum castings. Foundries and smelters often use hexachloroethane to degas the melt and improve its quality. Hexachloroethane introduces chlorine gas into the molten aluminum and removes hydrogen from the melt (Westberg et al. 1997). Emissions from this type of aluminum degassing have been shown to contain high concentrations of organochlorine compounds, OCS (780 ug/g) in particular (Westberg et al. 1997). The blood of nine aluminum foundry workers using hexachloroethane for degassing had significantly higher levels of OCS (54.6 ng/g) than the blood of 18 control subjects (0.7 ng/g) (Selden et al. 1997).

The waste water of an aluminum piston manufacturer using hexachloroethane and chlorine gas at high temperature (~600 °C) to remove hydrogen from the melt was analyzed. The waste water was found to contain OCS (230 ug/L), hexachlorobenzene (470 ug/L), octachloronaphthalene (130 ug/L), and decachlorobiphenyl (54 ug/L) (Vogelgesang 1986). Carbon from the clay-graphite molds used to form the pistons was surmised to react with the chlorine degassing agents to form OCS. These carbon molds needed to be replaced every two weeks. The alternative use of dichloroethane and Freon gas to degas the aluminum smelt produced similarly contaminated waste water and higher levels of OCS, HCB, and pentachlorobenzene in the resultant sewage sludge. However, the use of argon gas in the degassing of aluminum smelts apparently suffices as a substitute for chlorine or chlorinated degassing agents, without the undesirable generation of chlorinated organic compounds (Vogelgesang 1986).

Metals Degreasing

Similar to degassing, metals degreasing involves the use of organic solvents to remove grease, oils, waxes, carbon deposits, and tars from metal parts prior to assembly, painting, plating, heat treatment, and machining. The most commonly used solvents in open-top and in-line vapor cleaners are all chlorinated: methylene chloride, perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, and trichlorotrifluoroethane (CFC-113). Batch cold cleaners use little of these halogenated solvents. Metalworking operations and manufacturing facilities generally use open-top vapor cleaners, while in-line cleaners are more suited for manufacturing plants needing to clean a continuous stream of parts. In-line cleaners are commonly used in the cleaning of printed circuit boards, although these manufacturers may employ cold cleaning methods.

Both open-top and in-line vapor cleaners heat liquid solvent to boiling; the metal part is in a vapor zone placed such that the solvent gases condense on the cooler metal. The condensing solvent dissolves and removes impurities from the metal. Contaminated solvent and organic impurities accumulate in the sump and are either drained away or are routed through an adjacent still which extracts the grease/soil impurities and returns clean solvent to the vapor chamber

(Buonicore and Davis 1992). As in aluminum degassing, the reaction of chlorinated solvents with carbon deposits on the metal at elevated temperatures may generate OCS as a byproduct in the contaminated solvent drained from the machine or in the organic impurities that accumulate in the sump.

4.9 NONFERROUS METAL SMELTING/REFINING

Nickel

Oehme et al. (1989) reports the use of chlorine to extract and refine nickel from mineral ores. Waste water effluents and nearby sediments were found to contain chlorinated dibenzofurans, which were proposed to form under similar conditions as OCS and other chlorinated compounds. Kirk-Othmer (1996) describes roasting, smelting, and converting methods used to extract nickel from ores, but there is no mention of chlorine used in the extraction processes. Nickel may undergo refining by electrolytic methods to remove impurities and collect other metals, but again there is no indication that chlorine is involved in this process (Kirk-Othmer 1996).

Niobium and Tantalum

Niobium is used almost solely as an alloy in steel. Niobium and tantalum often occur together, combined with oxygen as a niobate or tantalate. Niobium does not occur in the free state. The metal must be extracted from mineral ores and refined. The stability of niobium ores requires high temperatures and powerful chlorine-containing oxidizers in a series of steps to retrieve metallic niobium.

One of the ore-extraction methods employed in the production of niobium is the reaction of chlorine gas with a mixture of ore and carbon at 500 to 1000 °C, according to the Kirk-Othmer Encyclopedia of Chemical Technology (1996). The combination of carbon and chlorine at high temperature makes niobium extraction processes suspected sources of OCS. Vogelgesang (1986) confirmed the release of OCS, as well as HCB and decachlorobiphenyl, from a niobium and tantalum production process in which chlorine gas was bubbled through the starting smelt material. A distillation operation used to separate various chlorides in the refining of niobium was also a source of these contaminants.

In 1993, there were five U.S. producers of niobium and tantalum, of which two, Shieldalloy Metallurgical Corporation and Cabot Corporation, processed niobium and tantalum from raw material to end product (Kirk-Othmer 1996).

Primary Copper Smelting

A chlorinating roasting process used in the production of red copper slag for gravel was identified as the source of OCS, and other chlorinated aromatics, at a German copper mine. In this roasting process, up to 8 percent sodium chloride was reacted with coal and copper slag at

high temperature (over 700 °C) (Döring et al. 1992). In the U.S., however, smelting methods used to produce copper from the sulfide ore do not incorporate chlorine and are not suspected as a source of OCS (Buonicore and Davis 1992).

Secondary Aluminum Smelting

Secondary aluminum smelting refers to the recovery and recycling of aluminum from new and used scrap aluminum. This process has been identified as one which forms OCS, in addition to other polychlorinated biphenyls, naphthalenes, chlorobenzenes, and chlorinated dioxins and furans (CDD/CDFs) (Döring et al. 1992).

Raw materials for aluminum recycling include obsolete metal from scrap yards, automobile shredding, aluminum copper radiators, post-consumer scrap, and slags and skimmings from primary aluminum processing, foundries, and die casters, as well as from secondary aluminum facilities (Buonicore and Davis 1992). A large part the post-consumer recycled material is used beverage cans, which contain interior coatings and sealants bearing chlorine. These chlorine-containing residues are generally separated from the aluminum in a delacquering process which vaporizes the organic contaminants prior to smelting. Alternatively, the cans may be processed as received, in which case the chlorinated organic compounds are vaporized as the scrap is melted in rotary furnaces. In either process, the conditions tend to favor the formation of OCS.

Other scrap being remelted typically contains surface coatings as well. Paint, dirt, oil, grease, lubricants, and coolants may be removed before being sent to the furnace by chip drying, scrap shredding, and “sweating”. Scrap aluminum of varying gauge and purity is melted in open-well charging or direct-charged reverberatory or rotary furnaces. Various types of pollution control measures are used to minimize fumes and particulate size, improve opacity, and reduce hydrochloric gas emissions (Buonicore and Davis 1992).

In the melting process, the tendency for aluminum to form oxides (dross) requires a mixture called “smelter’s flux”, consisting of roughly equal amounts of calcium chloride and sodium chloride with a small amount of a fluoride salt, to be added to the molten material to eliminate or reduce oxidation and the buildup of oxides from the walls. This process, then, is likely to be the step where OCS is formed. However, new technologies that do not use chlorine are being developed to recover aluminum from dross. These include centrifugation, flotation, plasma heating, and arc melting (Kirk-Othmer 1996).

Chlorine is also usually added to remove soluble gases and magnesium in a process labeled “demagging”. Magnesium reacts with the chlorine to produce magnesium chloride, which is pumped from the molten bath. A source of carbon from the residual coatings on scrap material combined with chlorine at elevated temperatures raises the potential for the formation of OCS in furnace emissions, in the molten bath, or in the magnesium chloride that is removed.

Secondary Copper Smelting

Secondary copper smelting involves the recovery and refining of copper and precious metals from scrap copper materials by smelting in blast furnaces. Scrap fed to smelting furnaces includes electronic telephones, plastic, bronze-, and iron-bearing copper scrap, brass and copper shot, precious metals, refinery byproducts, copper-bearing residues, converter furnace slag, anode furnace slag, and metallic floor cleaning material. Chlorine and carbon contained in the scrap, combined with temperatures of about 1200 °C, provide conditions favorable for formation of OCS, as well as other chlorinated aromatics (Döring et al. 1992). Although pollution control devices are used, there may be releases of OCS from this type of facility.

Secondary Lead Smelting

Metal alloy casting is another process identified by Döring et al. (1992) as employing conditions that result in formation of OCS. Secondary lead smelters cast metal alloys from the recovery of lead scrap. The source of chlorine may be PVC plastic separators used in lead-acid automotive batteries in the past. Lead-acid batteries constitute the major portion of lead recycled in secondary lead smelting furnaces, as the largest use of lead is in lead-acid batteries. Although PVC is no longer used in the manufacture of lead-acid batteries, PVC-containing batteries continue to be recycled. Incineration of PVC separators at temperatures of approximately 1260 °C may be the route by which OCS is inadvertently formed. Pollution control measures such as afterburners and baghouse dust collectors are typically employed at secondary lead smelting facilities for the control of organic compounds (Buonicore and Davis 1992). Though these may remove particle-bound OCS, and prevent its release into the atmosphere, the disposal of dusts and particulate matter may result in landfill loadings.

The processes described here for the recovery of aluminum, copper, and lead from scrap materials are pyrometallurgical (i.e., involve heating and melting of scrap metal). Due in part to increasing environmental legislation, hydrometallurgical or solution-based techniques are being pursued and implemented. These include electrolytic precipitation of a metal from a metal salt solution (Kirk-Othmer 1996). If graphite anodes are employed, the release of chlorine at the anode from a chloride salt solution would suggest hydrometallurgical methods of recycling scrap metal as suspected sources of OCS.

Titanium

The primary use of titanium is as titanium dioxide, a paint filler or pigment in surface coatings. It also finds uses in engines and airframes in aerospace and military applications and in commercial products such as golf club heads. The U.S. is one of the principal producers of titanium dioxide. Titanium ore, commonly called rutile or ilmenite, must be refined to titanium dioxide. High-grade ore is refined by chlorination, a process commercialized by DuPont. Low-grade ore is usually adapted for the chlorination process to a content of over 90 percent titanium dioxide and subsequently named synthetic rutile.

The chlorination process in the refining of titanium ore is a highly probable source of OCS (Vogelgesang 1986). This process involves the reaction of high-grade titanium ore or synthetic rutile with chlorine gas at 925 to 1010 °C to yield titanium tetrachloride and carbon monoxide (Kirk-Othmer 1996). This process, conducted in a fluidized-bed reactor, emits volatile chlorides and solid wastes. The reaction of chlorine and residual carbon at these temperatures is highly likely to produce OCS as a byproduct in the emitted volatiles or in the solid wastes.

The titanium tetrachloride is either oxidized at 985 °C to titanium dioxide or reduced to titanium metal. Titanium tetrachloride reduction processes do not appear likely to generate OCS, unless processing to remove impurities releases OCS formed during chlorination. In the reduction process, which is used for nearly all titanium metal produced today, the recycling of molten magnesium chloride using electrolytic magnesium reduction methods may potentially form OCS.

Vanadium

Vanadium is a metal used as an alloy additive to steel. It is found mainly in ores with other minerals such as iron, titanium and uranium, and is also found in petroleum. These materials are processed to obtain vanadium oxides which are further refined into vanadium metal and vanadium compounds. Ore processing involves a salt roasting process with sodium chloride or sodium carbonate at about 850 °C, followed by water/acid leaching and solvent extraction (Kirk-Othmer 1996). The similarity of this roasting process, which combines chlorine from sodium salt with carbon present in the mineral ore or the roasting kiln, to the method used to produce OCS-contaminated red copper slag indicates its potential to generate OCS.

Methods used in the manufacture of vanadium compounds are also suspected of generating OCS as a byproduct. Vanadium(V) oxytrichloride is produced from vanadium pentoxide by chlorination with charcoal at high temperature. Vanadium tetrachloride is produced by chlorination of vanadium compounds in the presence of carbon at about 800 °C (Kirk-Othmer 1996). By analogy to other processes, these reactions may also produce OCS.

4.10 ALUMINUM PLASMA ETCHING IN THE SEMICONDUCTOR INDUSTRY

Aluminum plasma etching is employed in the production of microchips and other microelectronic components in the semiconductor industry. Dry etching of aluminum conductors requires chlorine or chlorine-releasing compounds and irradiation with high-frequency radio waves to remove layers of material from the surface of a thin silicon wafer (Schmidt et al. 1995; Raabe et al. 1993). The etch reaction is performed under high-energy plasma conditions and results in organic waste products that must be removed by vacuum pump devices (Bauer et al. 1995). Samples of the waste products from a dry-etching reactor were analyzed by Raabe et al. (1993) and were found to contain OCS. Other studies of aluminum plasma etching processes used in the semiconductor industry confirmed OCS in the waste products, most notably in the solid wastes collected from the gas pipeline of the vacuum pump (Schmidt et al. 1995).

4.11 ETHYLENE DICHLORIDE/VINYL CHLORIDE PRODUCTION

Vinyl chloride is a major industrial chemical produced almost solely for the manufacture of polyvinyl chloride (PVC) and copolymers. Vinyl chloride is produced from ethylene and chlorine in a process termed “balanced” because it produces hydrogen chloride (HCl) in one step and consumes it in another. In this process, ethylene dichloride is first generated by direct chlorination of ethylene, followed by ethylene dichloride pyrolysis, which yields vinyl chloride and HCl. A subsequent step, oxychlorination, consumes the HCl from pyrolysis and generates ethylene dichloride and water. The net reaction is the production of vinyl chloride and water from ethylene and chlorine (Kirk-Othmer 1996).

The step involving the pyrolysis, or cracking, of ethylene dichloride to form vinyl chloride and HCl is suspected of generating OCS as a byproduct. This reaction mechanism makes use of free radical species in a chain reaction to crack ethylene dichloride and terminate with the formation of vinyl chloride. One byproduct in this chain reaction is propylene, which can react further with chlorine atoms to form OCS (Schulman and Klingele 1985). Benzene is another byproduct of ethylene dichloride pyrolysis (Kirk-Othmer 1996). As shown in Figure 4, aromatic compounds exposed to chlorinated radical intermediates are suspected of forming polychlorinated styrenes, including OCS (Schulman and Klingele 1985).

Under the authority of the Clean Air Act, the Clean Water Act, and RCRA, EPA regulates emissions from ethylene dichloride and vinyl chloride production facilities. There are no emissions released directly to the atmosphere, as regulations require emission sources to be enclosed and all emissions to be collected. Incineration is the commonly used to treat gaseous vent streams. Liquid streams and wastewater are stripped of trace organics, and solid waste is disposed of by such methods as incineration, landfill, and sludge digestion (Kirk-Othmer 1996).

4.12 INCINERATION PROCESSES

Model experiments have shown that OCS is formed during the incomplete combustion of chlorinated compounds such as polyvinyl chloride (PVC) and similar plastics, flame retardants, and household wastes. Ahling et al. (1978) reported 0-250 ng of OCS emitted per gram of PVC combusted at varying temperatures and transit times. Lahaniatis et al. (1989) confirmed the formation of OCS (1000-8000 ng/g of PVC) in the combustion of plastics and further concluded that all incineration processes involving chlorinated substances should be expected to form OCS. Organic wastes from chemical industries often contain chlorinated compounds. Water pipes, roof gutters, seat covers, tires, plastic containers, and even athletic shoes and textiles contain PVC. The eventual appearance of these products, unless they are recycled, in the waste stream makes them subject to accidental landfill fires and industrial, medical, or municipal waste incineration. Thus they become potential sources of OCS in the environment (Lahaniatis et al. 1989).

Boilers/Industrial Furnaces Burning Hazardous Waste

The burning of liquid hazardous waste as supplemental fuel in industrial boilers and furnaces is a suspected source of OCS as a byproduct in the incomplete combustion of chlorinated organic hazardous waste. The pollution of the North Sea environment due to the uncontrolled combustion of hazardous waste is well-documented (Lohse 1988; de Boer 1989; Dethlefsen et al. 1996). Industrial boilers and furnaces, however, are typically equipped with devices to control particulate and acid gas emissions, and the use of liquid hazardous waste is limited to 5 percent or less of the primary fuel.

Carbon Reactivation Furnaces

Carbon reactivation furnaces operate to restore absorptive activity and capacity to granular carbons used in pollution control and solvent recovery. Carbon reactivation furnaces desorb organic compounds to reactivate the spent carbon. Carbon reactivation may be conducted at commercial facilities using large multiple-hearth furnaces or on the site of activated carbon use with smaller scale furnaces (Buonicore and Davis 1992).

Many of the organic pollutants adsorbed are chlorinated compounds which will release chlorine at the temperatures reached in carbon reactivation furnaces (up to 1000 °C). This chlorine source is suspected of reacting with the activated carbon at high temperatures to form OCS. Although afterburners and water scrubbers are generally installed, CDD/CDFs have been measured in the emissions of carbon reactivation furnaces (Buonicore and Davis 1992).

Cement Kilns (Co-fired with Hazardous Waste)

The combustion of hazardous waste, burned as supplemental fuel, in cement kilns may be a source of OCS emissions. The production of cement requires high temperatures to heat the raw materials and trigger the necessary chemical reactions (pyroprocessing) in a cylindrical steel rotating furnace called a kiln. The temperatures required to induce pyroprocessing are 1,100 to 1,500 °C. Although coal or petroleum coke is primarily used to sustain these temperatures, the high cost of fossil fuels has resulted in the burning of solid and liquid organic hazardous waste as a supplemental fuel source to offset the cost of kiln operation. Automobile tires, used motor oil, sawdust, and scrap wood chips may also be used as supplemental fuel.

The composition of the hazardous waste burned as supplemental fuel by cement kiln operators is primarily waste oils, organic solvents, paints and coatings, and sludges from petroleum refineries. These wastes, spent organic solvents in particular, may be chlorinated. Before combustion, both liquid and solid hazardous waste are combined by injection or mixing with the primary fuel, which is usually coal. The combustion of chlorinated hazardous waste along with a source of carbon is similar to the incineration of chlorinated organic wastes on the North Sea, which has been shown to be a source of OCS.

Air pollution control devices are used on cement kilns to limit emissions of particulate matter and chlorinated dibenzodioxins (CDDs) and chlorinated dibenzofurans (CDFs) in the cement kiln dust. These devices consist of fabric filters and/or electrostatic precipitators. Quenching units are also sometimes added to reduce the flue gas temperature in the particle control device. This operation has been shown to significantly limit CDD/CDF formation at cement kilns. The air pollution control devices and quenching units have been successful in reducing CDD/CDF emissions, and it is expected that they also reduce potential OCS emissions. The pollution control dust, though, is sometimes used as a synthetic aggregate in construction applications; long-term sequestration of chlorinated by-products may not be assured with this practice (Kirk-Othmer 1996).

Drum and Barrel Reclamation Furnaces

Drum and barrel reclamation furnaces clean residues and coatings from previously-used 55-gallon steel drums. Drums from the petroleum and chemical industries are subjected to elevated temperatures to remove paint, interior linings, and previous contents of the drums as a conveyor moves the drum through the furnace. The residual contents of the drums are pre-drained at some furnaces, and the accumulated pre-drained liquids are fed back into the fuel stream. A fan blows the furnace exhaust gases to a high-temperature afterburner which achieves nearly complete reduction of CDD/CDF emissions. However, if not operating properly, the afterburner and the furnace cleaning operation are suspected sources of OCS.

The type of residual material in a drum varies depending on the source of the drums and may include volatile hydrocarbons, fuel oils, hazardous wastes, and pesticides. The amount of material remaining in a drum before it enters the furnace is estimated at zero to twenty pounds (Buonicore & Davis 1992). RCRA regulations require drums containing hazardous materials to be completely emptied and may not contain more than one inch of residual material. Drums holding pesticides or substances listed as “acutely toxic” by RCRA must be triple rinsed before being transported to a reconditioning facility. Resins, plastics, and gasket materials likely undergo incomplete combustion, and partially combusted polymeric materials may continue to smolder after moving out of the furnace on the conveyor. Therefore, fugitive emissions from these materials may be a source of OCS release.

Hazardous Waste Incineration

The formation of OCS, as well as hexachlorobenzene (HCB), during the incineration of organochlorine wastes is well-established (Ballschmiter et al. 1983). These studies are reinforced by findings of exceptionally high levels of OCS in the North Sea ecosystem when the ocean incineration of hazardous wastes was a common practice (Lohse 1988, Dethlefsen et al. 1996). The combustion vessels involved in ocean incineration on the North Sea lacked the technology employed today to insure complete destruction and/or control of chlorinated organics, and this hazardous waste incineration is expected to pose much less of a hazard.

Hazardous waste incinerators, such as those in the chemical processing industry, burn hazardous waste at temperatures of 982 °C or higher. Organic emissions, including OCS, are products of incomplete combustion, and their formation depends on the composition of waste feed and combustion conditions. Some organic compounds may also condense on fine particles. Hazardous waste combustion facilities are categorized as wet or dry scrubbing, or a hybrid of the two systems, depending on the type of pollution control equipment used. Wet systems are better for removing acid gas and hydrogen chloride emissions while dry systems are more efficient at lowering particulate emissions; hybrid systems combine the best of both wet and dry systems (Buonicore and Davis 1992). As OCS is not regulated and therefore not routinely monitored in hazardous waste incinerator emissions, the efficiency of pollution control systems in limiting OCS release is unknown. However, the releases of HCB and dioxins may give a fair estimate of OCS releases under various operating conditions.

Of particular concern are emissions from the incineration or thermal treatment of HCB and other chlorinated organic waste products that are known to generate OCS. According to 1996 Toxic Release Inventory (TRI) reports, chlorinated solvent manufacturers transfer tons of HCB and tetrachloroethane, for example, to waste management facilities where the chemical waste is incinerated or thermally treated.

Under the Clean Air Act, EPA has promulgated regulations to control the emissions from incinerators, cement kilns, and light-weight aggregate kilns that burn hazardous waste. The proposed regulations, expected to be finalized in December 1998, would limit emissions of hazardous air pollutants, and coincidentally would likely also reduce emissions of OCS.

Medical Waste/Pathological Incineration

Due to the infectious nature of wastes from hospitals, veterinaries, and medical research facilities, incineration is a practical option for disposal. The composition of medical waste varies, and representative analyses are difficult to obtain. Such wastes frequently have a high chlorine content, primarily from PVC, and contain carbon from pathological wastes and various other organic sources. To avoid problems caused by glass, metals, and ceramics that are not consumed during combustion, temperatures in medical waste incinerators (MWI) are kept relatively low (below 982 °C) (Buonicore and Davis 1992). As a result, compounds that are products of incomplete combustion (e.g. OCS and chlorinated dioxin) may be more likely to form. Tests performed by the State of California Air Resources Board on the uncontrolled emissions of eight MWIs showed an emission range for chlorinated dioxins of 106.5-2164.3 ng/m³ (Buonicore and Davis 1992). OCS can reasonably be assumed to have been present in these samples as well.

Some MWIs may not be equipped with best-available-technology air pollution control devices, since limits on stack emissions from MWIs were not established until the early 1990s. Modular furnaces, employed at most MWI facilities, do provide a secondary chamber where wastes from partial pyrolysis in the primary chamber are burned at higher temperatures to complete the destruction of organic contaminants. Longer residence times in the secondary

chamber also improve the thermal destruction of organic compounds. Under the Clean Air Act amendments, EPA set emission limits for new and existing MWIs in September 1997, with new units required to comply at start-up and existing units by September 2002. However, current OCS emission levels from MWIs are unknown, and only limited information exists for dioxin/furan releases.

Municipal Waste Incineration

Municipal waste combustion (MWC) units incinerate waste from households, institutions (excluding hospitals), and commercial and light industrial facilities, in addition to agricultural waste and sewage sludge (Buonicore and Davis 1992). Much of the waste burned in MWC units is chlorinated organic material, such as rubber, plastic, and treated wood. Agricultural waste, in particular, frequently contains chlorinated organic waste. As noted above, the combustion of chlorinated organic waste has been shown to result in the formation of OCS.

Although different types of incinerators are employed in municipal waste combustion, all facilities use electrostatic precipitators and other pollution control devices to meet strict emission limits, based on “maximum achievable control technology” (MACT), set by EPA. Temperatures are generally maintained at about 982 °C to complete combustion of organic compounds, and secondary chambers are used to reduce organic matter in flue gases. However, emissions concentrations vary widely among the different types of MWC units, and emission standards do not target OCS specifically but address organic emissions as total dioxins and furans (Buonicore and Davis 1992).

Petroleum Refining Catalyst Regeneration

Catalytic reforming is a process used at petroleum refineries in the blending of high octane gasolines and aviation fuels. The process requires an expensive platinum or platinum/rhenium catalyst, whose activity decreases as coke is deposited onto it under conditions of high temperature and pressure during the reforming process. Due to the high cost of the catalyst, it is regenerated by removing the coke deposits by burning at temperatures of 400-455 °C and then reactivating the catalyst through the use of chlorine or chlorinated compounds (e.g., methylene chloride, 1,1,1-trichloroethane, and ethylene dichloride) at temperatures of 455 to 538 °C. Chlorinated dioxins and furans have been detected in internal waste streams and wastewater sludges of petroleum refineries. Although the waste streams and stack gases from petroleum refineries have not been analyzed for OCS, its formation is a distinct possibility, as it is in any process involving carbon and chlorine at elevated temperatures (Schulman & Klingele 1985).

Environmental evidence supporting petroleum refining catalyst regeneration as a source of OCS can be found in the OCS-contaminated St. Clair River near petroleum refineries and petrochemical plants in the Sarnia area of Ontario. The OCS-contaminated Calcasieu River, at Bayou d’Inde, Louisiana, is likewise surrounded by an oil and gas field and impacted by petrochemical industries (Mallard & Ragone 1988; Pereira et al. 1988).

Although the primary sludges at petroleum refineries are considered hazardous wastes, EPA has recently issued a notice of proposed intent *not* to designate spent reformer catalysts as a hazardous waste under the Resource Conservation and Recovery Act (RCRA) (Federal Register, 1995b). EPA has indicated that the possibility of dioxin releases to the air during catalyst regeneration at petroleum refineries is a concern but discussion of OCS formation has not surfaced. Under the Clean Air Act, EPA will investigate the need to develop MACT standards for preventing the formation of CDD/CDFs at petroleum refining units. The significance of OCS formation in the treatment of catalytic reformer wastes has not been determined.

Scrap Electric Wire Recovery

Wire reclamation is the commercial practice of removing the insulation coating from wire products for sale of the reclaimed metal wire (typically copper) to secondary metal smelters. The insulating material that must be removed is usually plastics or chlorinated organic compounds. Incineration, once the common method of recovering scrap metal wire, would generate OCS, as has been shown in measurements of the combustion of PVC and chlorinated organic wastes. Minimal amounts of scrap wire continue to be incinerated at U.S. wire reclamation facilities; current practices involve mechanically chopping the scrap wire and separating the resulting particles by blowing the insulating material with gravitational settling of the heavier metal wire. Two facilities in the San Francisco Bay area were nonetheless recently discovered to thermally treat electric motors to recover electrical windings (BAAQMD 1996). OCS releases from operations that presently incinerate scrap wire in the U.S. are not known. Also unknown are the additional OCS releases from burning of scrap wire at open air sites and small-scale unregulated facilities.

Sewage Sludge Incineration

The incineration of sewage sludge is a suspected source of OCS due to the potential presence of chlorine in the furnace reacting with organic waste at temperatures as high as 800 °C. Sewage sludge burned in coastal communities, in particular, will have a higher sodium chloride (a source of chlorine) content from sea salt. The presence of chlorine is evidenced by the emission of hydrochloric acid that is formed during combustion (Buonicore and Davis 1992).

Pollution control devices at sewage sludge incinerators include wet scrubbers to control emissions of hydrochloric acid and other exhaust gases. Afterburners may be installed or combustion conditions adjusted to destroy volatile organic compounds in furnace gases. Dioxins and furans are suspected in the exhaust gases at sufficiently low levels not to merit concern, and the same may be assumed for OCS. It is anticipated that these compounds are controlled through efficient combustion practices (Buonicore and Davis 1992).

Uncontrolled Combustion of PCBs

Although the use of PCBs in new transformers has been banned in the U.S., existing transformers and capacitors still contain PCBs. As a result, PCBs in electrical equipment have

been burned in accidental fires and in the intentional combustion of PCBs in incinerators not approved for PCB combustion. Soot samples from a PCB transformer fire have been shown to contain CDD/CDFs, although the amounts vary depending upon the duration and intensity of the temperature and the PCB content of electrical equipment burned. Because this combustion is a source of CDD/CDFs, it is also likely to be a source of OCS.

4.13 POLYVINYL CHLORIDE (PVC) POLYMERIZATION

The polymerization of vinyl monomers by free radical initiation is a large-scale commercial process in the U.S. North American production of PVC by free-radical polymerization is approximately 6.5×10^9 kg (Kirk-Othmer 1996). Manufacturers of polyvinyl chloride (PVC), as well as ethylene dichloride and vinyl chloride monomer, recognize that CDD/CDFs are formed and released to the environment. The formation of OCS, however, is not certain. The U.S. vinyl industry has undertaken an extensive evaluation of various manufacturing and process control technologies for their potential to release CDD/CDFs to the environment. An interim report of emissions monitoring and product testing indicates that the vinyl industry is a minor source of CDD/CDFs emissions in the environment, and the same may hold for OCS, but is unknown (Kirk-Othmer 1996).

4.14 BLEACHED CHEMICAL WOOD PULP AND PAPER MILLS

The bleaching of wood pulp at pulp and paper mills is a suspected source of OCS due to the mixing of chlorine with a carbonaceous material (wood pulp). Approximately 60 percent of all chemical pulps are bleached to whiten the raw pulp, especially in the production of printing-grade paper (Buonicore and Davis 1992; Kirk-Othmer 1996). Chlorine and chlorine dioxide are two of the most important and most efficient bleaching agents. However in recent years, environmental concerns about the release of CDD/CDFs as byproducts of bleaching with chlorine have resulted in the emergence of new chlorine-free bleaching technologies. These include changes in processes, alternative bleaching agents, and new technologies such as the use of enzymes (biobleaching) (Kirk-Othmer 1996). Those pulp and paper mills which rely on older technologies, and are known to release dioxins in the effluent, are probably also producers of OCS.

4.15 COKE PRODUCTION

Coal is used to produce coke primarily for blast furnaces in the iron and steel industry. Coke manufacturing processes involve heating coal to temperatures of up to 1100 °C to distill out various components. Byproducts of this distillation are coke oven gas, ammonia, water, and sulfur. Due to chlorine present in the coal either naturally or from cleaning methods, OCS may be an additional byproduct of coking operations. In addition, some coking processes utilize chlorine at elevated temperatures to effect addition and substitution reactions; this treatment is highly suspect as a source of OCS (Kirk-Othmer 1996).

4.16 FUEL COMBUSTION

Combustion is essentially the same as incineration, although incineration usually refers to the burning of wastes for their destruction and disposal. The burning of fuel, virgin or waste, for the purpose of generating heat energy, which can then be converted into other forms of energy, is commonly labeled combustion. Combustion sources are suspected of releasing OCS for the same reason incineration sources have been identified—incomplete combustion of fuel containing carbon and chlorine. Theoretical flame temperatures are calculated to achieve complete combustion in fuel combustion units. The only products of complete combustion are carbon dioxide, water, nitrogen, oxygen, and sulfur dioxide. However, heat losses due to radiation, thermal conduction, and diffusion result in actual flame temperatures that are lower than theoretical temperatures (Kirk-Othmer 1996). As a result, products of incomplete combustion are likely to form.

Techniques to reduce pollutant emissions from fuel combustion can address the type and purity of fuel burned, combustion methods employed, or pollution control devices installed after the combustion process. Suggested methods for minimizing products of incomplete combustion in combustion systems are maintaining temperatures of at least 983 °C, ensuring complete mixing of fuels and oxidants, and eliminating cool zones in the furnace (Kirk-Othmer 1996). In the absence of these ideal conditions, HCB and dioxin are known to form; OCS is also suspected.

Coal Combustion

Utility and industrial boilers burn 80 percent or more of all coal for electric or steam power (Kirk-Othmer 1996). At the high temperatures attained in these boilers, coal is suspected of reacting with chlorine in coal to form OCS. OCS produced during combustion may adsorb to particles, either the bottom ash, fly ash, or stack particles retrieved by pollution control devices. The ash and particulate matter is reinjected into the combustion furnace, sold to Portland cement manufacturers, or landfilled.

The chlorine content of coal, as determined by Riggs et al. (1995), can vary from 300-390 mg/kg for subbituminous coal to 800-1,400 mg/kg for bituminous coal. Chlorine may be present naturally as chlorides in the coal, or it can potentially be introduced by chlorine or methyl chloride that are used in coal cleaning methods. Coal for power generation is frequently cleaned prior to combustion in an attempt to reduce emissions of sulfur oxides and nitrogen oxides (Kirk-Othmer 1996). Various types of pollution control devices employed at combustion facilities are used to reduce these emissions, as well as dioxin emissions (Riggs et al. 1995). These controls are also expected to control potential OCS emissions.

Oil Combustion

Residual oils burned in utility, industrial, and large commercial facilities are suspected of generating OCS on the basis of their CDD/CDF emissions. Residual oils contain impurities, including chlorine, since they are produced from the residue remaining after lighter fractions

(such as kerosene) are distilled from crude oil (Kirk-Othmer 1996). Used oil in particular, such as spent lubricating oil from diesel engines, contains higher amounts of chlorine. Utility boilers, electricity-generating plants, ships, ferries and barges, and residential stoves and furnaces are among the combustion units burning fuel oil for heat or power.

Vehicle Fuel Combustion

The presence of chlorine in fuel or oil additives (e.g., dichloroethane, pentachlorophenate), coupled with the incomplete combustion processes of gasoline and diesel engines makes the formation of OCS a possibility in motor vehicle exhaust. Ballschmiter et al. (1986) reported patterns of dioxin and furan congeners in used oil samples that were similar to patterns found in municipal waste incinerator emissions and fly ash. Due to similar mechanisms of formation for OCS and CDD/CDFs, OCS may be formed and emitted from motor vehicles.

Wood Combustion

The detection of CDDs and CDFs in residential wood-burning stoves and fireplaces forms the basis for suspecting residential wood combustion as a source category for OCS (Nestrick and Lamparski 1982; 1983). The full spectrum of chlorinated dioxin and furan congeners have been detected in fireplace soot, indicating that radical addition reactions are probably taking place and numerous products of incomplete combustion are present.

Chlorinated dioxins and furans have also been detected in industrial wood-burning furnaces and boilers (Buonicore and Davis 1992). Industrial wood furnaces include wood boilers used in the generation of electricity. Fuel burned in the industrial sector is commonly wood chips, bark, sawdust, and wood and agricultural wastes. However, demolition debris containing plastics, paint, creosote-treated wood, glues, synthetics, wire, cable, and insulation may be part of the wood fuel. Sludge and coal may also be burned in combination with wood residues. Facilities that store wood or lumber in sea water prior to combustion, or otherwise burn salt wood, will have a significantly higher content of chlorine in the wood and hence potentially higher OCS emissions. Chipboard, preservative-treated wood, and PVC-coated wood also have higher chlorine contents and a greater potential to emit OCS when combusted. Pulp mills, furniture manufacturers, and sawmills are just a few of the industrial wood-burning sources.

Current EPA regulations mandate low-emission combustion systems in space heating appliances, such as wood-burning stoves, fireplace inserts, and masonry heaters, built after 1990. Traditional open fireplaces and non-EPA-approved appliances are still in use, though. Regulations on industrial wood-burning furnaces and boilers are mainly concerned with particulate matter. To meet EPA's strict air regulations, air pollution control equipment on wood-fired boilers includes mechanical collectors in combination with wet scrubbers, wet and dry electrostatic precipitators, or fabric filters. The type of device used depends on the type of emissions, which in turn depends, among other factors, on the composition of wood/wood waste burned and the amount of fossil fuel burned with the wood waste. For example, the combustion of chloride-containing demolition debris requires acid gas removal equipment such as the use of

limestone. To the extent that these air pollution control devices remove particulate matter and chlorinated dioxins, they are probably effective in reducing OCS emissions, although OCS content of the emissions has not been specifically tested.

4.17 KRAFT RECOVERY BOILERS

The Kraft pulping process is the method by which the majority of wood is processed into paper and paperboard. In this process, after wood chips are cooked with sodium hydroxide and sodium sulfide, and the pulp is withdrawn, a black liquor remains. This spent liquor is concentrated and burned in recovery furnaces to recycle and regenerate the pulping chemicals. The combusted liquor contains carbon and chlorine from the wood pulp which are suspected of forming OCS, as dioxin emissions have been measured in this combustion process. Emissions from Kraft recovery furnaces typically pass through an electrostatic precipitator, thereby reducing particulate emissions. Emissions from Kraft pulp and paper mills will vary with the pulping processes and type of wood used (Buonicore and Davis 1992).

4.18 PESTICIDES MANUFACTURE

The use of lower chlorinated phenols (mono- to trichlorophenol) in the manufacture of pesticides and herbicides suggests that this industry may be a source of OCS emissions due to the methods employed in the production of chlorophenols. The manufacture and use of chlorophenol-based pesticides have been regulated extensively by EPA to control CCD/CDF contamination. As a result of these regulations, commercial production of chlorophenols in the U.S. has been limited to 2,4-dichlorophenol and pentachlorophenol. The main application of 2,4-dichlorophenol is in the synthesis of herbicides such as 2,4-D, diclofop-methyl and oxadiazon. The use of pentachlorophenol is restricted to wood preservation in the U.S. (Kirk-Othmer 1996).

The methods for producing 2,4-dichlorophenol include the direct chlorination of phenol and/or a monochlorinated phenol using chlorine or sulfuryl chloride (SO_2Cl_2) with chlorination promoters and stabilizers. In as much as this reaction is known to form CDD/CDFs, it is, by analogy, suspected of forming OCS (Kirk-Othmer 1996).

4.19 PENTACHLOROPHENOL PRODUCTION FOR WOOD PRESERVATION

Pentachlorophenol, or PCP, is manufactured in the U.S. solely for use in the long-term (25-40 years) protection of wood. Soaking wood in a 3-5 percent solution of PCP protects the wood from fungi (Kirk-Othmer 1996). Pentachlorophenol is produced by the direct chlorination of phenol in the presence of catalysts with progressively increasing temperature. The production of PCP, like that for 2,4-dichlorophenol, is suspected of forming OCS as a byproduct in trace amounts (Kirk-Othmer 1996).

4.20 PRIMARY ALUMINUM

The Alcoa Smelting process involved the electrolysis of aluminum chloride using carbon electrodes to release chlorine and produce aluminum (Schulman & Klingele 1985). Between 1976 and 1982, one aluminum plant reported excessive maintenance and repair costs and formation of polychlorinated biphenyls in the cell as major drawbacks to the Alcoa process. A more recent process description indicates that chlorine is no longer involved in the production of aluminum (Buonicore and Davis 1992). Today, electrolysis of alumina (aluminum oxide) in a Hall-Héroult cell dominates the industry (Kirk-Othmer 1996). The extent to which the Alcoa process is still in use may indicate the potential for OCS releases.

A greater potential source of OCS in the aluminum industry is not the primary production of aluminum, but the electrolytic purification used to obtain high-purity aluminum. The electrolytic cells consist of three layers through which aluminum is electrochemically transported from bottom to top. The bottom layer contains impure aluminum plus an alloy (usually copper) serving as the anode. The intermediate layer contains an electrolyte which accumulates impurities as chlorides and fluorides. The top layer contains graphite cathodes and purified aluminum that has migrated through the layers. A carbon cell bottom and graphite blocks are used to make the electrical connection to the metal alloy anode. The cells operate at 950-1000 °C and 20,000 A. The presence of chlorine in contact with graphite blocks at these operating conditions provides a potential mechanism for formation of OCS.

4.21 RUBBER TIRE MANUFACTURING

The suggestion that tire manufacturing emits OCS is based on the fact that the process has been identified as a source of HCB in that emissions inventory. The specific step at which one or both chemicals would be formed is unknown at this time. A generic discussion of the process follows.

Several steps in the tire manufacturing process, show potential for generating OCS (including the mixing, milling, extruding, calendaring, curing, and cementing operations). Carbon black is one of the ingredients in the rubber compound used to manufacture various components required in the production of rubber tires. Natural rubber contains chlorine. The mixing step combines raw materials, including carbon black in a mixer with the use of vulcanizing agents, plasticizers, and initiators. During milling, the rubber compound is heated to a fluid in preparation for extruding. Extruding shapes the rubber into profiles by forcing the hot fluid through dies. The calendaring process uses hot rubber from the mills and forms it into fibers or thin sheets of rubber and rubber-coated materials. Curing presses and molds the various components of a tire together under high temperature and pressure. Prior to curing, an uncured tire is sprayed with a lubricant so that the tire does not adhere to the mold during curing. Cementing is the use of adhesives or solvents at various stages of tire building to improve adhesion of rubber components and prevent separation prior to curing. Due to the high temperature and presence of organic materials, OCS may be formed.

4.22 OTHER POTENTIAL SOURCES

The production of synthetic graphite by the pyrolysis of petroleum and coke is a suspected source of OCS due to the high furnace temperatures employed (2200-3000 °C) and the presence of chlorine in the starting materials (Schulman and Klingele 1985). Due to processes of incineration, other suspected sources of OCS include non-hazardous waste burning cement kilns, landfill fires, and pulp and paper mill sludge incineration.

4.23 POTENTIAL OCS SOURCES IN THE GREAT LAKES BASIN

The industrial processes identified above suggest that several facilities in the Great Lakes basin may be past or current releasers of OCS. The location, status, and associated industry of facilities located in the Great Lakes basin are listed in Table 3. This table also includes a few additional industrial sites in other regions of the U.S. (e.g. Lake Charles, LA), but this table is by no means intended as a comprehensive list for the whole U.S.

Table 3. Potential Industrial Sources of OCS in the Great Lakes Basin (with some large U.S. facilities also noted)

Industry	Facility	Location	Status
Chlor-alkali/chlorine	DuPont Olin Corp. RMI Company International Minerals & Chemical Corp. Hooker Chemical Hooker Chemical Mobay Pennwalt Corp. Pennwalt Corp. PPG Industries Dow Chemical Dow Chemical Dow Chemical	Niagara Falls, NY Niagara Falls, NY Ashtabula, OH Ashtabula, OH Tacoma, WA* Montague, MI Baytown, TX* Niagara Falls, NY Wyandotte, MI Tacoma, WA* Lake Charles, LA* Midland, MI Sarnia, Ontario, CAN	
Chlorinated Solvents	Polysar Ltd. Dow Chemical	Sarnia, Ontario, CAN Sarnia, Ontario, CAN	
Landfill Disposal	Detrex Chemicals Dow Chemical CECOS, Inc. flyash disposal landfill Reserve Environmental Services	Ashtabula, OH Sarnia, Ontario, CAN Niagara Falls, NY Fields Brook ,OH Ashtabula, OH	old covered lagoons landfill leachate contains OCS near State Road receives wastes from potential OCS sources

Table 3. Potential Industrial Sources of OCS in the Great Lakes Basin (Continued)

Industry	Facility	Location	Status
Magnesium Production	Dow Chemical Magcorp Norsk Hydro Magcan	Freeport, TX* Rowley, UT* Becancour, Quebec, CAN Aldersyde, Alberta, CAN	Shut down in 1991. Still inactive in 1993.
Metals Degreasing/Degassing	Metal foundries		
Nonferrous Metal Smelting/Refining			
- Niobium and Tantalum	Union Carbide	Niagara Falls, NY	
- Secondary Aluminum Smelting			
-Secondary Copper Smelting			
- Secondary Lead Smelting			
- Titanium	Gulf Western Resources Group SCM Corp. Teledyne Wah Chang Timet Alta Titanium (Johnson-Matthey)	Ashtabula, OH Ashtabula, OH Albany, OR* Henderson, NV* Salt Lake City, UT*	
- Vanadium	Union Carbide, Metals Div.	Niagara Falls, NY	
Semiconductor	Microelectronics producers		
Ethylene Dichloride/Vinyl Chloride Production			
Boilers/Industrial Furnaces Burning Hazardous Waste			
Carbon Reactivation Furnaces			

Table 3. Potential Industrial Sources of OCS in the Great Lakes Basin (Continued)

Industry	Facility	Location	Status
Cement Kilns (Co-fired w/ Hazardous Waste)			
Drum and Barrel Reclamation Furnaces			
Hazardous Waste Incineration	CECOS, Inc. CWM Chem-Security Detrex Chemical Dow Chemical Encycle/Texas Inc. Gulf Western landfill Occidental Chemical Corp. Reserve Environmental Services Tricil Ltd.	Niagara Falls, NY Chicago, IL Swan Hills, Alberta, CAN Ashtabula, OH Midland, MI Corpus Christi, TX* Ashtabula, OH Niagara Falls, NY Ashtabula, OH Sarnia, Ontario, CAN	
Medical Waste/Pathological Incineration			
Municipal Waste Incineration	Municipal waste incinerators		
Petroleum Refining Catalyst Regeneration			
Scrap Electric Wire Recovery			
Sewage Sludge Incineration			
Uncontrolled Combustion of PCBs			
PVC Polymerization	General Tire & Rubber Co. SHINTEC Geon FPC Oxychen Borden Georgia Gulf Vista	Ashtabula, OH	

Table 3. Potential Industrial Sources of OCS in the Great Lakes Basin (Continued)

Industry	Facility	Location	Status
Bleached Chemical Wood Pulp & Paper Mills			
Cement Kilns (Non-Hazardous Waste Burning)			
Coke Production			
Coal Combustion			
Oil Combustion			
Vehicle Fuel Combustion			
Wood Combustion			
Kraft Recovery Boilers			
Landfill Fires			
Mono- to Tetrachlorophenol Production in Pesticides Manufacture	Dow		2,4-dichlorophenol production
Pentachlorophenol Production for Wood Preservation	Idacon Occidental Chemical Corp. Vulcan	U.S. North Tonawanda, NY U.S.	
Primary Aluminum			
Pulp & Paper Mill Sludge Incineration			
Synthetic Graphite Production	Airco-Speer	Niagara Falls, NY	
Tire Manufacturing	General Tire & Rubber	Ashtabula, OH	

*Indicates facilities outside of the Great Lakes Basin.

4.24 OCS EMISSIONS ESTIMATES BASED ON DIOXIN AND HCB INVENTORIES

Although numerous industrial processes can be identified as potential sources of OCS, no national emissions estimates exist. To obtain an approximation of OCS emissions from various

source categories, U.S. emissions inventories of HCB and dioxin were consulted as a basis from which to calculate preliminary release estimates for OCS. Similarity of OCS formation to formation of HCB and chlorinated dioxins was discussed in Section 4.2 above.

The emissions inventories by source category for HCB and chlorinated dioxins are shown in Table 4. This HCB inventory is taken from the final report of the Emission Inventory Data for Section 112(c)(6) Pollutants, released in April 1998; the dioxin inventory is taken from USEPA's draft Inventory of Sources of Dioxin in the United States, released in April 1998. As described earlier, the average ratio of OCS to HCB in sediments was compiled from available literature reports. These data are listed in Table A-1, Appendix A. This ratio was applied to the HCB inventory values to obtain estimates of OCS releases. Similarly, the ratio of 17 dioxin congeners to OCS was determined from various fish samples where both were measured. The available data are listed in Table A-2, Appendix A. The average ratio was computed, and then adjusted by the relative BAF values of 2,3,7,8-TCDD and OCS to obtain an emission factor to apply to the dioxin inventory data. The estimated OCS emission by source category are listed in the third column of Table 4. As shown in Table 4, on the basis of this inventory method, approximately 4,000 lb of OCS may be emitted in the U.S. yearly. (Total estimated U.S. HCB and dioxin inventory emissions are 4,597 lb/yr and 6 lb TEQ/yr, respectively. This emission rate, though, does not include estimates from several known OCS sources (such as magnesium production), as they have not been documented as sources in either the dioxin or HCB inventory.

Table 4. Potential National OCS Emissions by Source Category

	1995 U.S. Dioxin Emissions (g TEQ/yr) ^a	1990 U.S. HCB Emissions (g/yr) ^b	Potential U.S. OCS Emissions (g/yr)
DOCUMENTED OCS SOURCES			
Chlor-alkali/Chlorine Production	*		*
Chlorinated Solvents/Chlorobenzenes Production		526,630	78,995
Landfill Disposal	*		*
Magnesium Production	*		*
Metals Degreasing/Degassing	*		*
Nonferrous Metal Smelting/Refining			
- Nickel	*		*
- Niobium and Tantalum	*		*
- Secondary Aluminum Smelting	17		11,101
- Secondary Copper Smelting	541		353,273
- Secondary Lead Smelting	1.63		1,064
- Titanium	*		*
- Vanadium	*		*
Semiconductor/Aluminum Plasma Etching	*		*
HIGHLY PROBABLE OCS SOURCES			
Ethylene Dichloride/Vinyl Chloride Production	*		*
Incineration Processes			

Table 4. Potential National OCS Emissions by Source Category (Continued)

	1995 U.S. Dioxin Emissions (g TEQ/yr) ^a	1990 U.S. HCB Emissions (g/yr) ^b	Potential U.S. OCS Emissions (g/yr)
- Boilers/Industrial Furnaces (haz. waste burning)	0.38		248
- Carbon Reactivation Furnaces	NEG		NEG
- Cement Kilns (co-fired with haz. waste)	153		99,909
- Drum & Barrel Reclamation Furnaces	0.23		150
- Hazardous Waste Incineration	5.7		3,722
- Medical Waste/Pathological Incineration	477		311,481
- Municipal Waste Incineration	1100		718,300
- Petroleum Refining Catalyst Regeneration	*		*
- Scrap Electric Wire Recovery	*		*
- Sewage Sludge Incineration	6		3,918
- Uncontrolled Combustion of PCBs	*		*
PVC Polymerization/Production	*		*
SUSPECTED OCS SOURCES			
Bleached Chemical Wood Pulp & Paper Mills	45		29,385
Cement Kilns (non-haz. waste burning)	17.8		11,623
Coke Production	**[10]		**[6.5E+03]
Fuel Combustion			
- Coal Combustion (industrial/utility)	72.8		47,538
- Oil Combustion			
- Residential	**[10]		**[6.5E+03]
- Industrial/Utility	9.3		6,073
- Vehicle Fuel Combustion			
- Unleaded	6.3		4,114
- Diesel	33.5		21,876
- Wood Combustion			
- Residential	62.8		41,008
- Industrial	29.1		19,002
Kraft Recovery Boilers	2.3		1,502
Landfill Fires	**[1000]		**[6.5E+05]
Pesticides Manufacture		415,044	62,257
- Mono- to Tetrachlorophenol Production	NEG		NEG
Pentachlorophenol Production for Wood Preservation	25,000		16,325,000 ^d
Primary Aluminum	*		*
Pulp & Paper Mill Sludge Incineration	c		c
Synthetic Graphite Production	*		*
Tire Manufacturing		394,178	59,127
TOTAL in g/yr			1,885,666
TOTAL in lbs/yr			4,157

Table 4. Potential National OCS Emissions by Source Category (Continued)

	1995 U.S. Dioxin	1990 U.S. HCB	Potential U.S. OCS
	Emissions (g TEQ/yr) ^a	Emissions (g/yr) ^b	Emissions (g/yr)

a Source: Draft Inventory of Sources of Dioxin in the United States (air or applicable media emissions).

b Source: Final Report of Emission Inventory Data for Section 112(c)(6) Pollutants, released April 1998.

Estimates converted from pounds to grams.

c Included within total for Wood Combustion.

d This estimate relates to contamination levels put into product, primarily utility poles, and is not included in the total.

NEG = Expected to be negligible (i.e., less than 1 gram per year) or nonexistent.

* Insufficient data exist for making an emission estimate.

** Estimates were too uncertain to include in the inventory. A number in square brackets indicates the order of magnitude estimate for this source.

5.0 CONCLUSIONS

On the basis of existing evidence, it cannot be confirmed that OCS is not used or released from sources that enter the Great Lakes Basin. Studies from the 1980s report OCS at various levels at sites within the Great Lakes Basin, depending on the proximity of the samples collected to apparent sources of OCS in the environment. The most recent data available have identified OCS in sediment and mayfly nymphs at the mouth of the Detroit River (Drouilliard et al. 1996) and in lake trout of eastern Lake Ontario (Huestis et al. 1996). Information on present OCS levels in other areas of the Great Lakes is not available. Several sites where high concentrations of OCS were reported previously have not been revisited: the Ashtabula River at Ashtabula, Ohio; tributaries of Lake Huron; the upper St. Marys River (Lake Superior); and the Niagara River area. OCS concentrations in Lake Michigan, past or present, are almost entirely unknown.

OCS levels in lake trout have been tracked in eastern Lake Ontario from 1977 to 1993 (Huestis et al. 1996). Early declines in concentrations have leveled off to a stable level of OCS at this location. From 1986 to 1993, the levels of OCS in lake trout have been 29-44 ng/g with an average of 35 ng/g. For the average adult (70 kg) consuming 16 g of fish per day (USEPA, 1996) that has average OCS levels of 35 ng/g, the daily intake of 8 nanograms of OCS per kilogram of body weight per day (ng/kg bw/day) is significantly lower than Health Canada's Minimum Risk Intake (MRI) limit for OCS from food of 310 ng/kg bw/day. For sport fishermen consuming an average 22 g of fish per day (USEPA, 1996), the daily intake of OCS rises to 11 ng/kg bw/day.

Health Canada's MRI is established on the best information currently available, albeit limited to one study. This estimated OCS intake from food is due only to fish consumption. A recent study of local foodstuffs grown or raised in the vicinity of an OCS-emitting chlorinated solvent producer showed that OCS was present in lamb meat, olives, celery, and lettuce (Otero and Grimalt 1994). Clearly, foods other than fish may have measurable OCS levels. Health risk limits have not been established for children. If a 10-fold reduction in Health Canada's MRI for adults were used to estimate a MRI for children, then the estimated intake of OCS for breast-fed infants (13 ng/kg bw/day) would approach a child risk level of 31 ng OCS/kg bw/day.

Insufficient data is the main difficulty encountered in estimating or quantifying OCS emissions from potential sources. On the basis of process similarities, approximations of OCS emissions have been derived from emissions estimates for HCB and dioxin. These data are only a tentative gauge of OCS emissions for several potential sources and are presented only for discussion purposes. This estimate suggests a potential emission rate of 4,000 pounds of OCS per year in the U.S. This estimate does not include emissions from several known sources of OCS. Emission estimates for these known sources could not be quantified because these sources are not included in either the HCB or dioxin inventories.

The need to take further action to reduce OCS emissions is unclear. Though highly persistent and bioaccumulative, its toxic effects are largely unknown, and the actual releases from potential sources have not been quantified.

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APPENDIX A

LITERATURE-DERIVED OCS/HCB AND OCS/DIOXIN RATIOS

APPENDIX A

LITERATURE-DERIVED OCS/HCB AND OCS/DIOXIN RATIOS

An average ratio of OCS to HCB concentrations, used to determine potential national OCS emissions by source category from national HCB emissions estimates, was derived from ratios of OCS to HCB concentrations reported in the literature. Table A-1 lists the ratios used in this calculation, along with the year of measurement, location, and literature reference.

Table A-1. Ratios of OCS to HCB Concentrations Reported in the Literature

Ratio	Year	Location	Reference
0.04	1980	Sediments of Lakes Huron, St. Clair, and Erie	Oliver and Bourbonniere 1985
0.12	1982	Sediments of Lakes Huron, St. Clair, and Erie	Oliver and Bourbonniere 1985
0.25	1982	Sediments of Lakes Huron, St. Clair, and Erie	Oliver and Bourbonniere 1985
0.08	1982	Sediments of Lakes Huron, St. Clair, and Erie	Oliver and Bourbonniere 1985
0.07	1982	Sediments of Lakes Huron, St. Clair, and Erie	Oliver and Bourbonniere 1985
0.21	1985-1987	Sediments of Elbe Estuary, near Hamburg	Krieg and Kausch 1993
0.27	1985-1987	Sediments of Elbe Estuary, near Hamburg	Krieg and Kausch 1993
0.10	1985-1987	Sediments of Elbe Estuary, near Hamburg	Krieg and Kausch 1993
0.13	1985-1987	Sediments of Elbe Estuary, near Hamburg	Krieg and Kausch 1993
0.16	1985-1987	Sediments of Elbe Estuary, near Hamburg	Krieg and Kausch 1993
0.14	1985-1987	Sediments of Elbe Estuary, near Hamburg	Krieg and Kausch 1993
0.11	1985-1987	Sediments of Elbe Estuary, near Hamburg	Krieg and Kausch 1993
0.11	1985-1987	Sediments of Elbe Estuary, near Hamburg	Krieg and Kausch 1993
0.11	1982-1986	Suspended sediments from Lake Ontario ecosystem	Oliver and Niimi 1988
0.11	1981	Bottom sediments in Lake Ontario	Oliver and Niimi 1988
0.01	~1988	Bottom sediments in Bayou d'Inde area of LA near industrial outfall	Pereira et al. 1988
0.17	~1988	Suspended sediments from Bayou d'Inde area of LA near industrial outfall	Pereira et al. 1988
0.25	~1996	Sediment from Trenton Channel of Detroit River	Drouilliard et al. 1996
0.25	~1996	Sediment from Trenton Channel of Detroit River	Drouilliard et al. 1996
0.23	~1996	Sediment from Trenton Channel of Detroit River	Drouilliard et al. 1996
0.29	~1996	Sediment from Trenton Channel of Detroit River	Drouilliard et al. 1996
0.29	~1996	Sediment from Trenton Channel of Detroit River	Drouilliard et al. 1996
0.03	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.02	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.13	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.14	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.06	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.05	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983

Table A-1. Ratios of OCS to HCB Concentrations Reported in the Literature (Continued)

Ratio	Year	Location	Reference
0.08	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.16	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.07	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.18	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.19	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.13	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.27	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.36	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.14	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.22	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.05	1981	Sediment from mouth of Niagara River, Lake Ontario	Darham & Oliver 1983
0.15	average		

An average ratio of OCS to dioxin concentrations, used to determine potential national OCS emissions by source category from USEPA's draft *Inventory of Sources of Dioxin in the United States*, was derived from ratios of OCS to dioxin concentrations reported in the literature. To be consistent with the U.S. inventory, dioxin/furan concentrations were first converted to toxic equivalency concentrations (TEQs) using internationally adopted toxic equivalency factors (TEFs). The TEQ describes the cumulative toxicity of mixtures of dioxin/furan congeners. Toxic equivalency concentrations (TEQs) were calculated by multiplying individual congener concentrations by their assigned TEFs and summing the TEQ concentrations for all dioxin congeners reported for a particular sample. An OCS to dioxin ratio was then obtained by dividing the OCS concentration by the summed TEQ concentration for each sample, and an average of all ratios was calculated. Table A-2 lists the OCS to dioxin ratios determined from measurements reported in the literature, along with the number of dioxin congeners reported, year of measurement, location, and literature reference.

Table A-2. Ratios of OCS to Dioxin Concentrations Reported in the Literature

Ratio	# Congeners	Year	Location	Reference
11,007	17	1986	bream from Elbe River, Germany	Luckas & Oehme 1990
8,428	17	1986	bream from Elbe River, Germany	Luckas & Oehme 1990
7,034	17	1986	bream from Elbe River, Germany	Luckas & Oehme 1990
2,468	17	1986	bream from Elbe River, Germany	Luckas & Oehme 1990
13,483	17	1986	bream from Elbe River, Germany	Luckas & Oehme 1990
8,484	average			
653	scaled by relative BAF values for OCS and 2,3,7,8-TCDD			
Dioxin concentrations converted to toxic equivalency (TEQ) using factors adopted by international convention (U.S. EPA, 1989).				

Since the OCS and dioxin measurements reported in these literature references were taken from living tissues, the greater tendency for OCS to bioaccumulate had to be taken into account. To do this, the average OCS to dioxin ratio was scaled by the ratio of bioaccumulation factors (BAFs) for dioxin (9×10^6) and OCS (117×10^6) (USEPA 1995). The final ratio used to determine potential OCS emissions from USEPA's draft *Inventory of Sources of Dioxin in the United States* was the BAF-scaled ratio of OCS to dioxin of 653.